

Viscosity Aging of Poly(vinyl chloride) Plastisol: The Effect of the Resin Type and Plasticizer Type

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ABSTRACT: The viscosity of freshly prepared poly(vinyl chloride) (PVC) plastisol increases with time, and this phenomenon is called *viscosity aging*. The increase is rapid in the beginning and slows down to a quasistable value, but a very slow increase continues. The phenomenon may be a result of either the deagglomeration of agglomerated particles or the dissolution of low-molecular-weight PVC into the plasticizer. In this work, two typical commercial resins were used, one containing friable agglomerates and the other containing nonfriable agglomerates. With the friable-agglomerate resin, about 40% of the initially present agglomerates deagglomerated, whereas the viscosity increased in a week to twice the initial value. With the nonfriable-agglomerate resin, very fine and very low molecular weight particles, about 3% of all the particles, dissolved into the plasticizer in

2 days. The effect of the plasticizer type on the viscosity aging through deagglomeration was investigated with four plasticizers and three plasticizer blends. The emulsifiers used for polymerization, and retained through drying, affected the aging in the beginning. On the other hand, the viscosity after 1 week was free from the effect of the emulsifier and was affected only by the plasticizer type. With the exception of two blends, the 1-week viscosity was quantitatively related to the dielectric constant divided by the molecular weight of the plasticizer. For the plasticizer blends, one of the plasticizers could have a dominant effect on the promotion of deagglomeration. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 448–464, 2005

Key words: ageing; resins; viscosity

INTRODUCTION

Poly(vinyl chloride) (PVC) plastisol is a suspension of fine particles of PVC in a plasticizer. When a plastisol is freshly made, its viscosity increases with time. This is called *viscosity aging*. The rate and magnitude of the increase in the viscosity depend on how the PVC resin is made. They also depend on the solvent power of the plasticizer and the temperature. As for the latter, the aging is much more significant at 40°C than that at room temperature. However, with the exception of a plasticizer with a high solvent power, the viscosity increase gradually diminishes with time at room temperature. In general, the viscosity increase is most significant in the beginning and becomes very small after a certain period of time. There is an indication that a major portion of the PVC resin is not touched by the plasticizer after several months to years of storage.^{1,2} With a PVC resin containing friable agglomerates, the major cause of viscosity aging is the deagglomeration of PVC particles.² With this type of resin, larger particles, that is, agglomerates, are needed to lower the viscosity of the plastisol at room

temperature. However, upon heating, they must deagglomerate as quickly as possible. This is because, in certain processes, a rapid increase in the viscosity (and modulus) with the temperature is needed, and this is achieved through a rapid swelling of particles with a plasticizer. In general, the friability of an agglomerated particle is adjusted according to the projected use conditions of the resin. For example, there is a nonfriable grade of PVC, which also provides viscosity aging, but in this case, a small amount of low-molecular-weight resin may be dissolving.

One of the objectives of this work is to investigate viscosity-aging mechanisms, which are related to the resin type, which has either friable or nonfriable agglomerates. The other objective is to seek a quantitative relationship for viscosity aging between the properties of commercial plasticizers and resins containing friable agglomerates.

EXPERIMENTAL

Samples

The PVC samples are listed in Table I. The samples of the plasticizers and their blends are listed in Table II. Plastisols were prepared via mixing with a laboratory-type plastisol mixer (Hobart Manufacturing Co., Troy, OH).

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TABLE I
PVC Samples

Resin designation	Trademark ^a	Characteristic
A	Geon 121	Containing friable agglomerates
B	Geon 120×283	Containing friable agglomerates
C	Geon 124A	Containing nonfriable agglomerates

^a Products of PolyOne Corp. (Avon Lake, OH).

Viscosity measurements

A spindle rheometer was used with a V spindle. The viscosity was monitored at preassigned times at certain intervals after the plastisols were prepared.

RESULTS AND DISCUSSION

Viscosity aging of the resins containing friable agglomerates

The particle size distribution of resin A is reproduced in Figure 1, which shows the bimodal nature of the distribution. The larger particle fraction, having a median diameter of approximately 15 μm , consists of the agglomerates, and the smaller fraction, having a diameter of 1 μm or less, consists of the primary particles. In a previous publication,² the morphology of agglomerated particles was examined in detail with the use of a scanning electron microscope. Some ag-

glomerates appeared friable, and others could be fused more firmly.

Several examples were presented² to show deagglomeration during storage or by stirring. Microscopic observations during the viscosity aging of this resin in di-2-ethylhexyl phthalate (DEHP) did not show any change in the primary particle size. In a fixed field, the deagglomeration of agglomerated particles was noticed.⁵ In DEHP, which was separated from plastisol, no PVC was detected.⁶

The viscoelastic behavior of plastisols, made with various ratios of agglomerated (coarse) and primary (fine) particles, was also reported before.² From these data, a quantitative relation was established later between the fine/coarse ratio and storage modulus or loss modulus.⁷ This relationship is used in the calculation of the extent of deagglomeration and the resulting viscosity increase.

The data for viscosity aging are listed in Table III.

The general trend in viscosity aging is that the increase in the viscosity levels off at about 1 week, and there is a very slow increase thereafter. The trend was pointed out first by Iida and Furuya in 1968.⁸ They attributed the initial rapid increase to deagglomeration and the subsequent slow increase to the dissolution of a small amount of the polymer. However, no data were given to substantiate the interpretation. The slow increase may also be caused by deagglomeration.

TABLE II
Plasticizers and Plasticizer Blends

Plasticizer	Parts per 100 parts of resin by weight	η (mPa s) ^a	ε ^b	δ ^c	ε/MW	$\delta/\text{MW}^{\text{d}}$
1 DHP	55	55	5.62	9.00	0.0168	0.0266
2 DEHP	55	112	5.15	8.23	0.0132	0.0211
3 DTDP	55	335	4.06	8.45	0.0077	0.0159
4 DEHP/S160 ^a	25		5.15	8.23		
	30		6.45	9.88		
blend		96	5.87 ^e	9.13 ^e	0.0173 ^f	0.0269 ^f
5 DEHP/S148 ^g	25		5.15	8.23		
	30		6.65	9.03		
blend		71	5.98 ^e	8.67 ^e	0.0142 ^f	0.0198 ^f
6 DOZ	55	35	4.04	8.44	0.0098	0.0205
7 DEHP/G54 ^h	35					
	20		4.2 ³			
blend		400	4.8		0.0087 ⁱ or 0.0151 ^j	

DHP = di-isohexyl phthalate; DTDP = di-tridecyl phthalate; DOZ = di-octyl azelate.

^a For a plasticizer or blend containing 5 parts of epoxidized soybean oil and 3 parts of barium cadmium zinc stabilizer.

^b Values are independent of frequency at 1–100 kHz; values at 1 kHz are listed here except S148 at 10 kHz.

^c A very wide range of values are listed in the original table;⁴ to be consistent, the values referred to Small by the authors are taken.

^d Butyl benzyl phthalate.

^e Mass-based average of either ε or δ of the component plasticizers.

^f Mass-based average of either ε/MW or δ/MW of the component plasticizers.

^g Decyl diphenyl phosphate.

^h Poly(ethylene glycol sebacate).

ⁱ MW = 3420

^j MW = 228 (monomeric molecular weight)

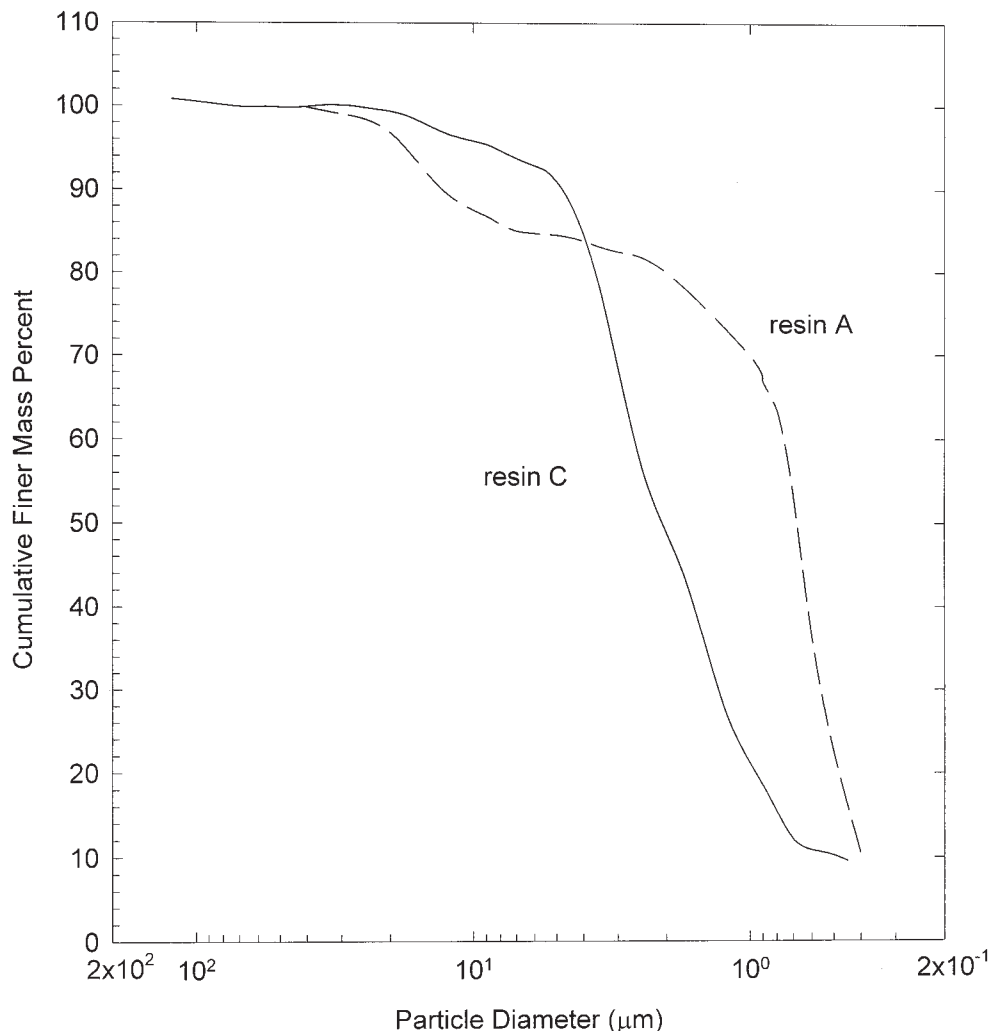


Figure 1 Particle size distributions of resin A and resin C.

An inspection of the data of Table III shows that, in 2 weeks, the viscosity increased to twice the initial value for all three samples, regardless of the particle concentration. The ratio of fine particles to coarse particles after 2 weeks of aging was previously reported to be 82/18.² Then, the initial fine/coarse ratio may be estimated to be

TABLE III
Viscosity Aging of PVC-DEHP Plastisol^a with Resins Containing Friable Agglomerates

Sample Particle volume fraction Rheometer speed (rpm)	1 0.532		2 0.478		3 0.434	
	2	20	2	20	2	20
Viscosity (Pa s) at 23°C						
Initial	11	8.7	5.0	3.9	3.5	2.75
1 day	14	10.4	6.5	5.0	4.5	3.4
1 week	24	16.6	10	7.4	6.0	4.5
2 weeks	25	17.0	11	8.1	7.0	5.2

^a Containing 3 phr epoxidized soybean oil and 2 phr barium cadmium zinc stabilizer.

70/30 for a viscosity increase of twice the original value. This calculation was made through the relationship between the viscosity and the ratio of fine particles to coarse particles.⁷ It appears that out of 30% of the originally present agglomerates, 12% were friable.

Viscosity aging of the resins containing nonfriable agglomerates

The particle size distribution of resin C is also shown in Figure 1. The distribution of this resin is broad and

TABLE IV
Viscosity Aging of PVC-DEHP Plastisol with Resins Containing Nonfriable Agglomerates

Aging time (h)	Apparent viscosity (Pas)	
	2 rpm	20 rpm
3.8	7.0	5.7
23.7	8.4	6.9
49.8	9.0	7.2
93.8	9.2	7.2
333.7	11.2	9.0

TABLE V
Calculation of the Change in η_r of Plastisol After the Partial Dissolution of the Particles

	Before dissolution	After dissolution
ϕ	0.500	0.485
Degree of packing ($\phi/\phi_c, \phi_c = 0.60$)	0.833	0.808
$\log \eta_r$	3.22	2.88
η_r	1660	760
Ratio	1.00	0.46

monomodal with a small amount of fine particles (ca. 20% were 1 μm or smaller). There was a very small change in the particle size distribution over a period of 94 h. Even after 335 h (14 days), there was only a relatively small increase in the fine particle fraction. However, in the corresponding period, there were noticeable increases in the viscosity (Table IV).

With this resin, the viscosity increased, after 2–4 days, to about 1.3 times the original value (at 3.8 h). Thereafter, there was a slow increase for 2 weeks (333.7 h).

Referring to the data of Table IV, we can observed that the increase in the viscosity leveled off after about 2 days of aging. In the corresponding period, the particle size distribution changed slightly. Particles smaller than 0.45 μm apparently disappeared. The amount corresponded to about 3% of the total particles.

The following calculations were used to determine if the dissolution of these fine particles was responsible for the increase in the viscosity.

A relationship between the relative viscosity (η_r) of the PVC plastisol and its particle volume fraction (ϕ) is given by a universal curve of the following form:⁹

$$\log \eta_r \sim \phi / \phi_c \tag{1}$$

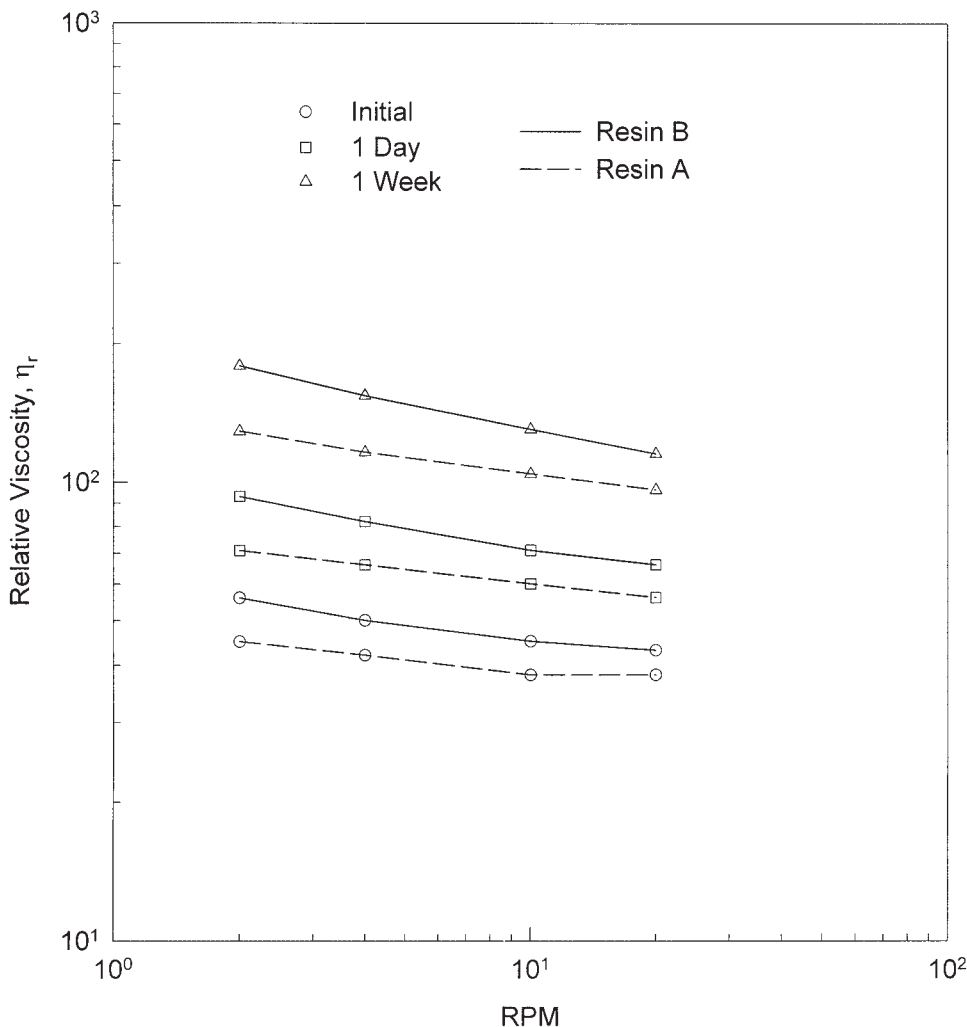


Figure 2 Viscosity shear rate (rpm) relationships of resin B and resin A plastisols, exhibiting a viscosity increase with time. The different markings indicate the periods of aging.

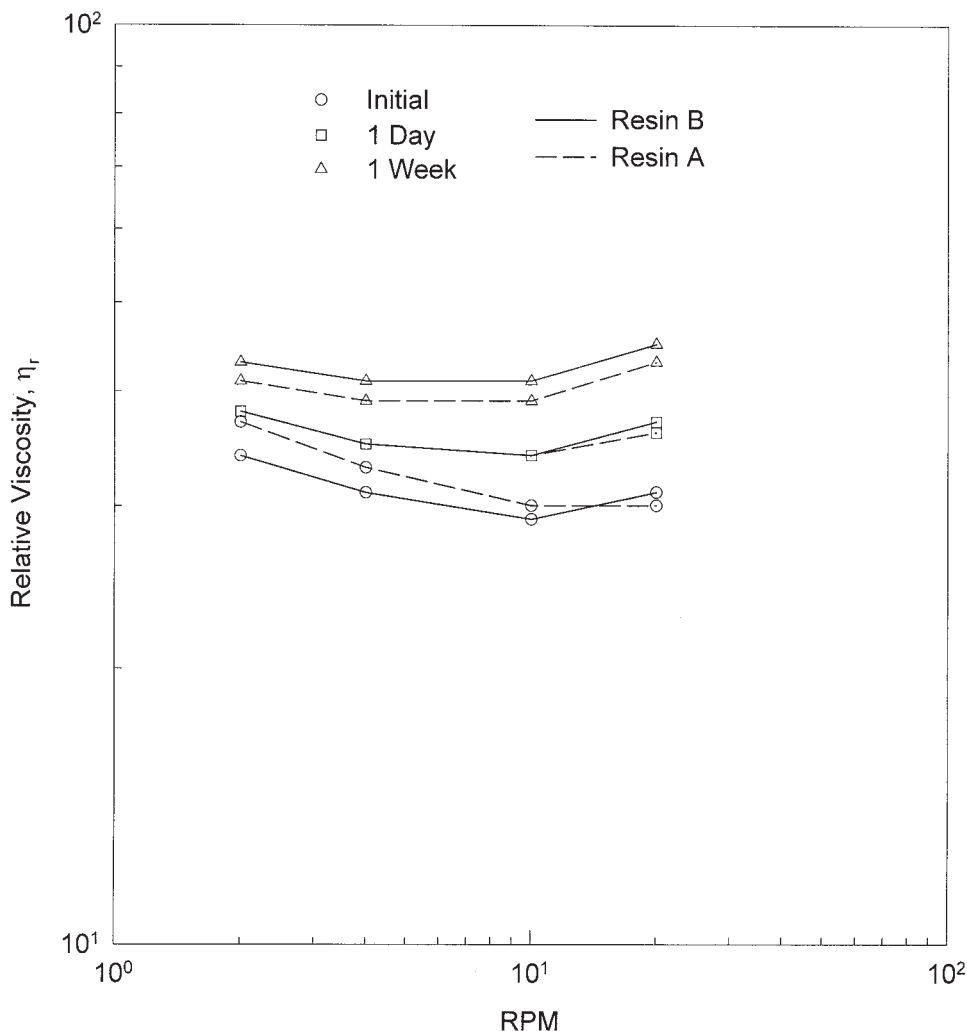


Figure 3 Pseudoplastic flow and dilatant flow observed with plastisols containing a high-viscosity plasticizer and resin B or resin A. The different markings indicate the periods of aging.

η_r is the ratio of the plastisol viscosity (η) to the viscosity of the plasticizer medium (η_s):

$$\eta_r = \eta / \eta_s \quad (2)$$

ϕ_c is the maximum volume fraction of the particles for the tightest packing, toward which the viscosity of the plastisol approaches infinity.

In this example, the dissolution of 3% of the particles changed ϕ from 0.500 to 0.485. In principle, ϕ_c also changes because the manner of particle packing depends on the particle size distribution. However, a 3% decrease in the fine particle fraction produced only a negligible change in the parameter.⁷ Therefore, it was assumed that ϕ_c remained constant at a value of 0.60. The data of the quantitative analyses are presented in Table V.

Although η_r decreased to 0.46 of the initial value, the observed viscosity increased 1.3 times (Table IV). Therefore, η_s must have increased to $2.8 = 1.3/0.46$ times the initial value because of the dissolution of 3% of the particles.

The concentration dependence of the dilute solution viscosity can be obtained as follows:

$$\eta_{s,sp}/c = [\eta] + k[\eta]^2c \quad (3)$$

$$\eta_{s,sp} = \eta_{s,r} - 1 \quad (4)$$

where $\eta_{s,sp}$ is the specific viscosity (as defined by eq. [4]) of plasticizer containing dissolved PVC, $[\eta]$ is the intrinsic viscosity, k is a constant, c is the polymer concentration (g/100 mL of solution), and $\eta_{s,r}$ is the relative viscosity of plasticizer containing dissolved PVC. The volume fraction of 3% of the polymer dissolved into 100% of the plasticizer DEHP led approximately to $c = 4.0$, with the density of PVC taken to be 1.4.

Combining eqs. (3) and (4) leads to

$$\eta_{s,r} = 1 + [\eta]c + k[\eta]^2c^2 \quad (5)$$

where the value of k depends on the solute-solvent pair. The k value for the PVC-DEHP system is not

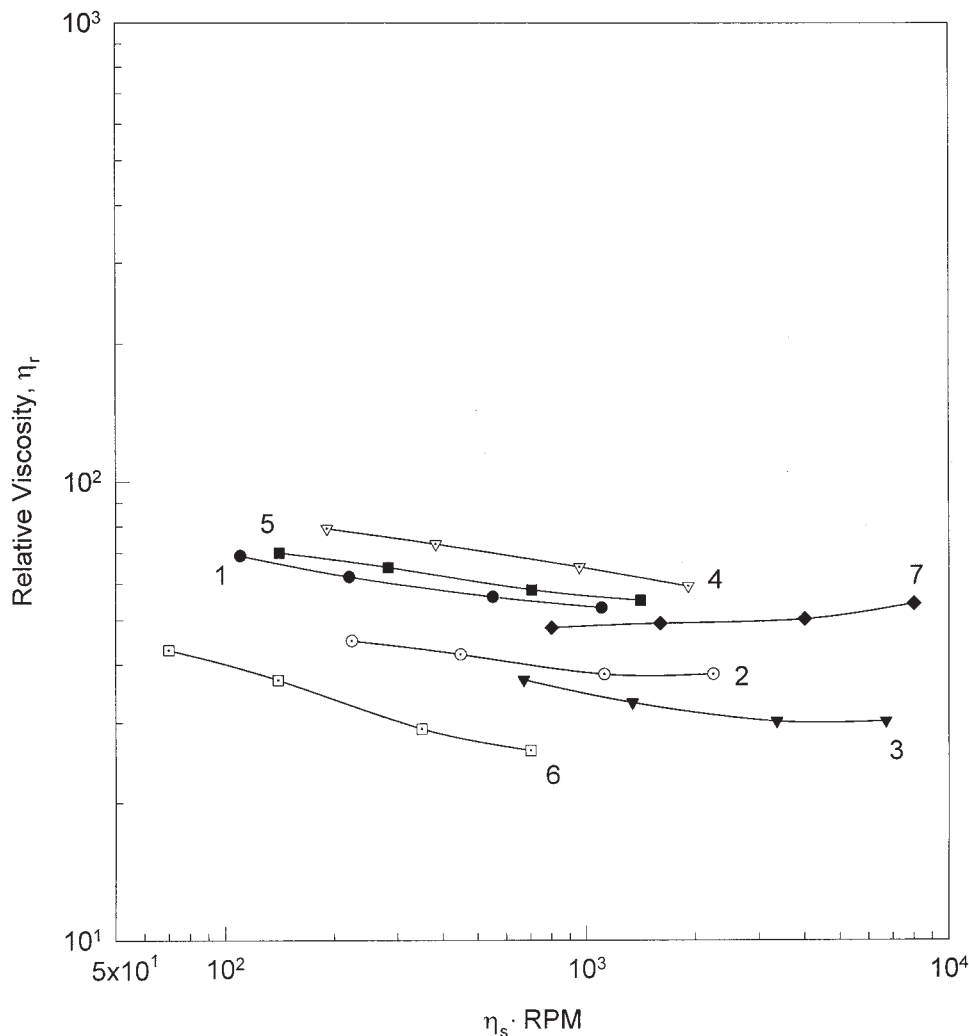


Figure 4 Effect of η_s on flow curves. A general trend is indicated of pseudoplastic flow at lower shear rates and dilatant flow at higher shear rates.

known. Because of the approximate nature of this calculation, the third term is assumed to be negligible for the moment. Then, from the values of $\eta_{s,r} = 2.8$ and $c = 4.0$, $[\eta]$ is found to be 0.45. When the third term is taken for the calculation, the estimate of the $[\eta]$ value is smaller. The commercial PVC resins for the plastisol application have $[\eta]$ values of 0.7–1.4.¹⁰ The conclusion from this analysis is that the fine particles, which dissolved during aging for 2 days, were composed of very low-molecular-weight polymer. In addition to the higher solubility due to the lower molecular weight (MW), the lower crystallinity and the lower crystalline stability of the low-molecular-weight polymer must have caused the dissolution of the fine fraction.

Viscosity aging and plasticizer type

Four plasticizers and three binary blends of plasticizers were used to include a wide variety of commonly use formulations (Table II).

The PVC samples were resin A and resin B, which contained friable agglomerates. These resins differed in the kind of emulsifier, which was carried over from polymerization through drying.

Figure 2 presents plots of η_r of the plastisol made with DEHP (plasticizer 2 of Table II) as a function of the speed (rpm) of a spindle rheometer. Although the speed of the spindle rheometer is not exactly proportional to the shear rate,¹¹ for this discussion it is adequate to regard it as a relative measure of the shear rate. Therefore, these curves are the steady-state flow curves, showing the pseudoplastic nature of the flow, that is, a decrease in the viscosity with an increase in the shear rate.

There are four significant observations: (1) for a given period of aging, resin B increased in η more than resin A; (2) the difference in the viscosity between the two resin systems somewhat increased for a longer period of aging; (3) in this comparison, the difference was larger at a lower shear rate (rpm); and (4) the difference in η_r for the two initial flow curves indi-

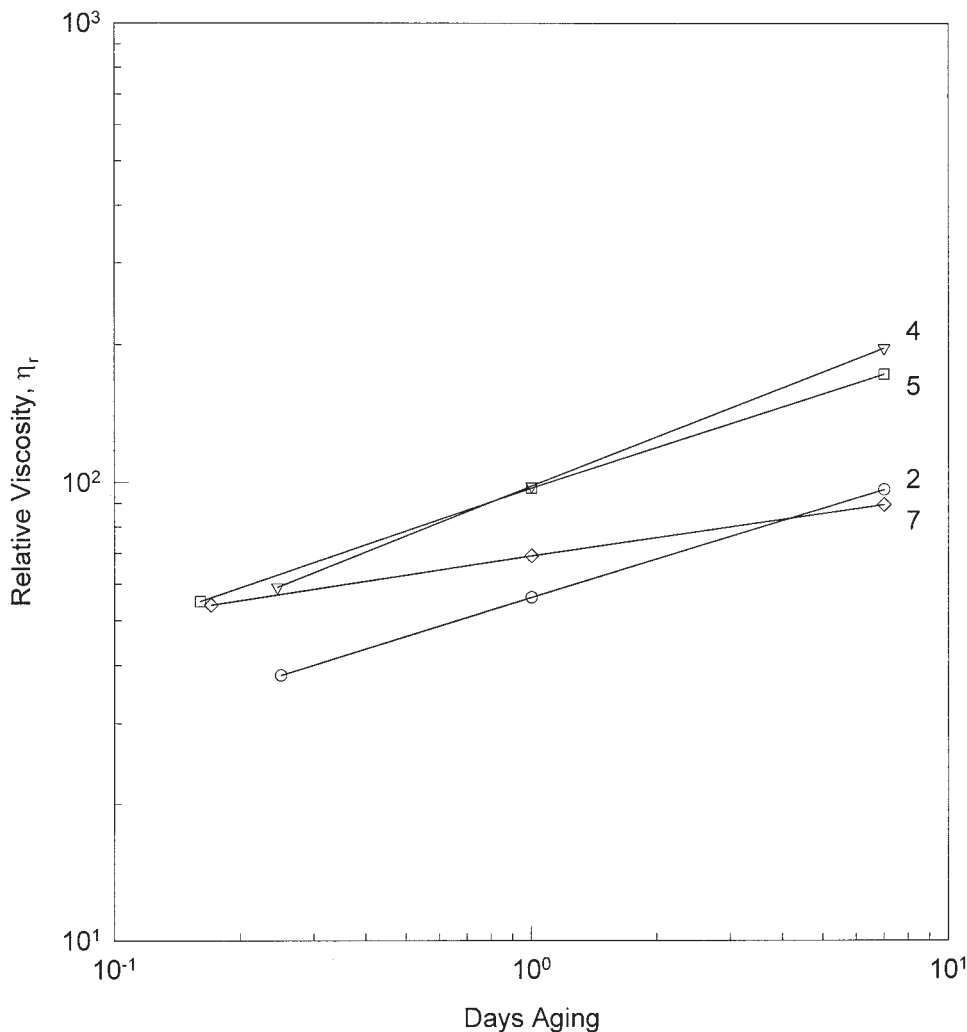


Figure 5 Effect of the plasticizer type on the viscosity aging.

cated that deagglomeration had already started during the preparation of the plastisols.

Because the increase in the viscosity was entirely a result of deagglomeration,² the first two observations indicated that resin B deagglomerated more quickly than resin A. Because the deagglomeration generated more fine particles, the increased amount of fine particles raised the viscosity more at lower shear rates than at higher shear rates, as known from our previous work.¹²

With all seven plasticizers listed in Table II, the plastisols made with resin B increased the viscosity more quickly than those made with resin A, as stated in the first observation. However, in other production lots, the latter deagglomerated more quickly than the former. This difference in the rate of deagglomeration presumably came from the adjustment of, or variation in, the drying conditions of the resin. The second observation was not necessarily common among all the samples. The effects of the plasticizer types on the rate and extent of the viscosity increase were somewhat more complex and are discussed later.

Effect of the plasticizer viscosity

With five of the seven plastisols, the flow curves showed pseudoplastic flow. However, the plastisols made with plasticizers 3 and 7 gave pseudoplastic flow only at a lower the speed (rpm); at a higher speed (rpm), the flow was dilatant. That is, the viscosity increased with an increase in the shear rate (rpm), as shown in Figure 3.

Plasticizer 3 and plasticizer blend 7 had very high viscosity, which influenced the particle motions in flow. In general, with a given medium, as the shear rate becomes higher, the slower motions of the particle are no longer able to participate in the flow. The higher viscosity of the medium accentuates the effect. In other words, if the observations had been extended to a higher speed (rpm), the dilatant behavior would have been observed with all seven samples, or when the time frame of the observation is fixed, the lower viscosity of the medium brings up the response of longer relaxation times, whereas the higher viscosity of the medium highlights the response of shorter re-

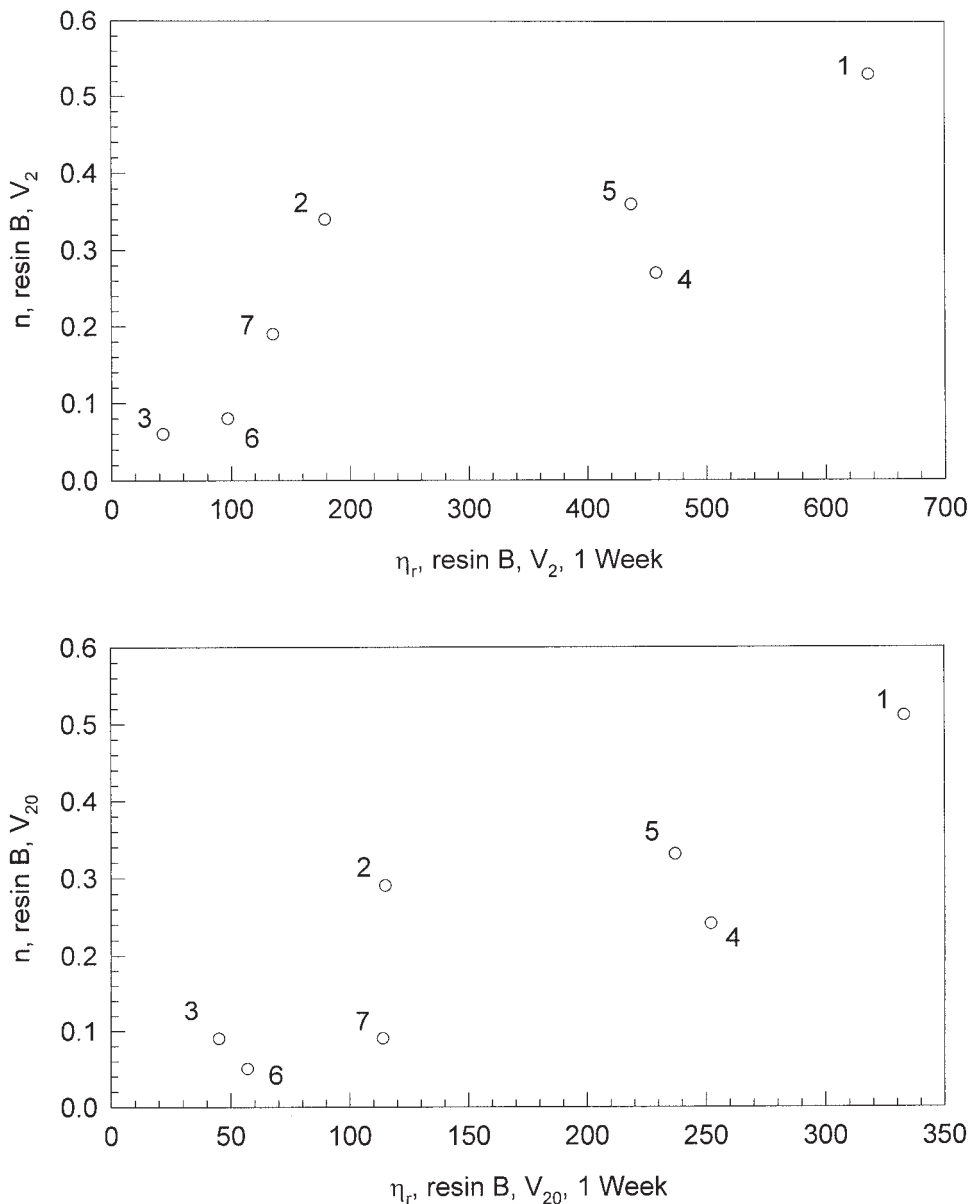


Figure 6 *n* versus η_r after 1 week. No unique relation is shown.

laxation times. This effect (technique) was applied to a polymer solution for the purpose of expanding the frequency range from the observation made at narrower frequency range.¹³ The method was also applied to colloidal dispersions.¹⁴ Previously, Hoffman¹⁵ recognized this effect of the viscosity of the medium on the nature of the shear rate dependence. By multiplying the shear rate by the viscosity of the medium, he brought flow curves of PVC plastisols with different plasticizers into a comparable range of relaxation times. His PVC was a model system with monodispersed particles, and the plastisols were presumably free of the aging effect.

Even though these data include the aging effect, the trend of the medium viscosity in the flow curves can

be seen in Figure 4, in which the η_r data are plotted as functions of the speed (rpm) multiplied by η_s . This figure implies that at a lower value of η_s times the speed (rpm), the flow was pseudoplastic, and at a higher value, the behavior became dilatant for all the samples.

It follows that the viscosity aging may have to be compared at a constant value of η_s times the speed (rpm) instead of a constant speed (rpm). However, we use η_r at a constant speed (rpm) for convenience. The viscosity is almost the same, regardless of whether the value is taken at a constant speed (rpm) or a constant value of η_s times the speed (rpm). The flow curves are very flat, and η_s times the speed (rpm) can be estimated for these examples.

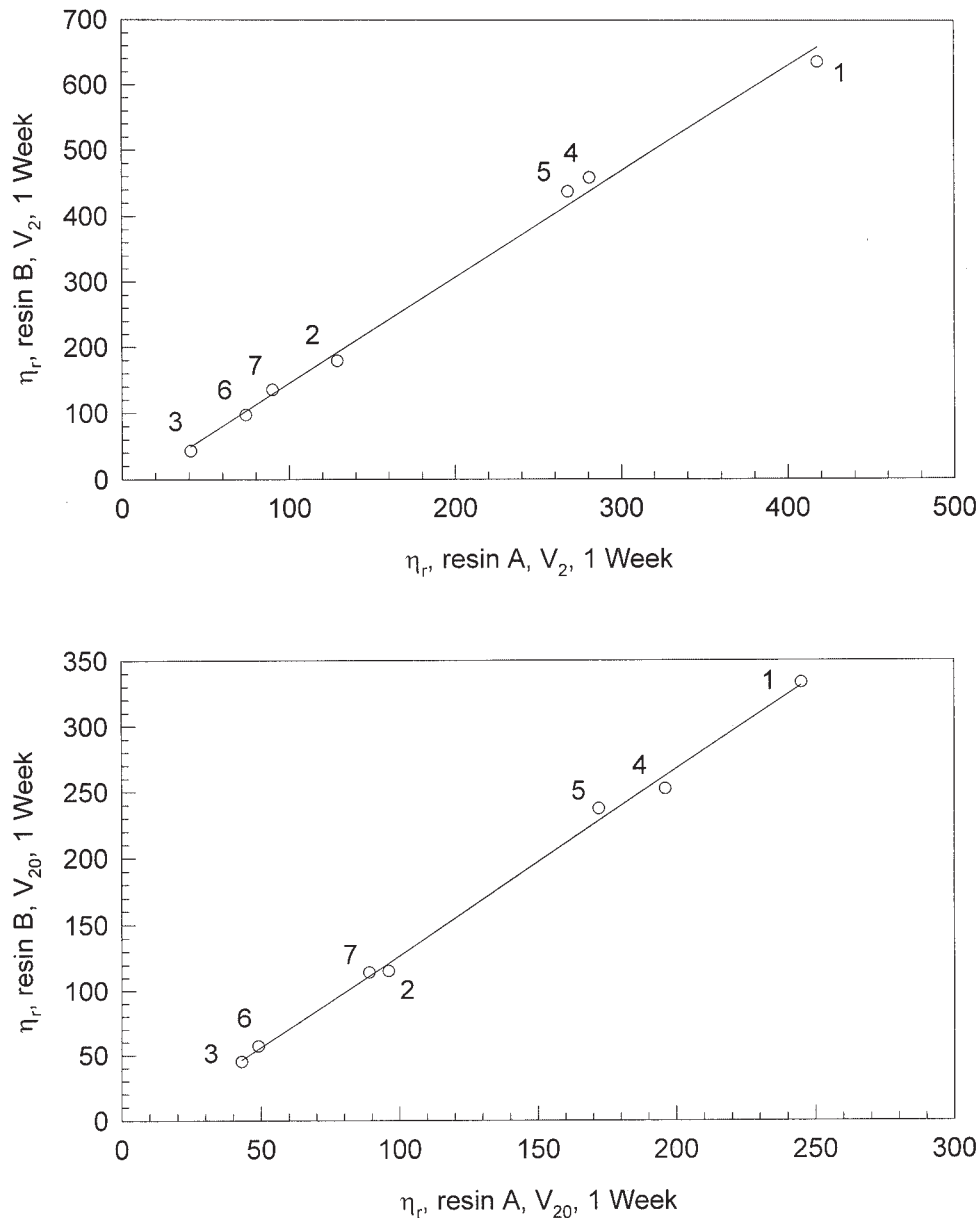


Figure 7 η_r after 1 week. It is not affected by the different emulsifiers used in the polymerizations of two different resins.

Treatment of the aging data

Figure 5 presents the aging data of resin A, measured with a V spindle at 20 rpm. The η_r data at 1 day and 1 week of aging are plotted on a log-log scale because in our experience such a plot of η_r versus the aging time gives a straight line with a good approximation. When the initial value of the viscosity is plotted on this straight line, the initial time is estimated to be about 0.2 day. The scattering of the data around 0.2 day is actually not an error in time but an error in viscosity. Because the deagglomeration is very fast in the beginning, the viscosity data have a somewhat larger error.

From this plot of the aging data, two parameters may be extracted to represent the aging behavior. One

is the slope (n) for the rate of aging, and the other may be the 1-week viscosity for the extent of aging.

A question is whether the higher rate of aging gives a higher extent of aging or not. If it does, the viscosity after 1 week must have a unique relation with n . In the plot shown in Figure 6, the data points are scattered extensively. This indicates that the two parameters are not completely dependent on each other. Therefore, two parameters are necessary for describing the aging phenomena.

Effects of the emulsifiers

A question is whether or not the interaction between the plasticizer and emulsifier affects the aging. Be-

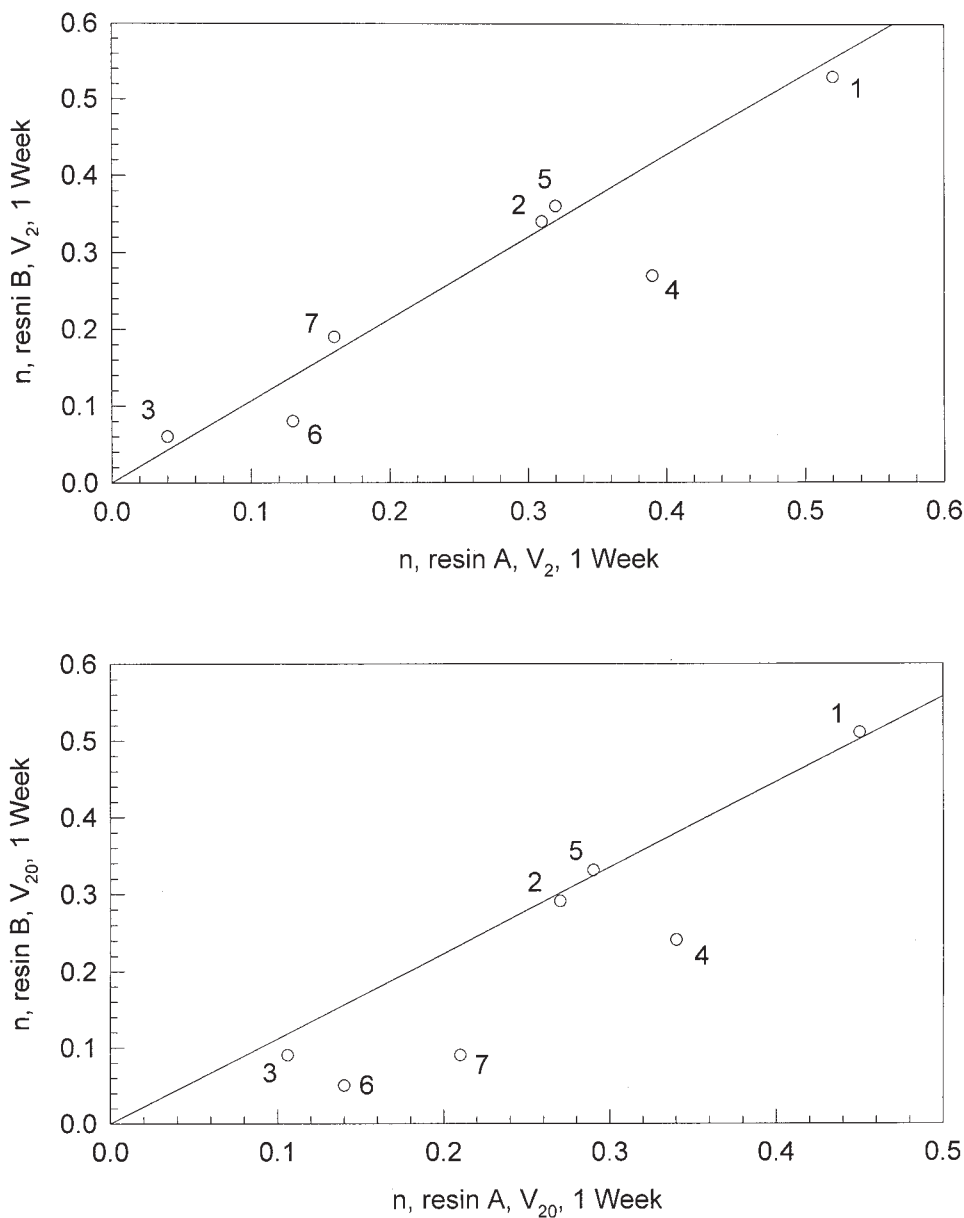


Figure 8 Dependence of n on the emulsifier type used in the polymerization.

cause the two resins in question have different kinds of emulsifiers, contrasting their aging data may provide the answer. In Figure 7, η , at 1 week of aging of one resin system is plotted against that of the other resin system for both plastisols containing the same plasticizer. All the data at 20 rpm, for different plasticizers and plasticizer blends, fall on one line, and this indicates that the emulsifier type does not affect the 1-week viscosity. This is also approximately true at 2 rpm.

In Figure 8, the values of the indices (n) are contrasted for the two resin systems. The points for phthalate plasticizers (samples 1–3) and a plasticizer blend (sample 5) are on one line. The data for azelate (sample 6) and for two plasticizer blends (samples 4 and 7)

deviate from the line, and this indicates that the emulsifier affects the rate of aging. That is, the emulsifier influences the viscosity aging in the beginning but may be extracted before 1 week.

Interaction between PVC and the plasticizer

Usually, three different parameters have been used to represent the PVC–plasticizer interaction: the Flory–Huggins interaction parameter (χ), dielectric constant (ϵ), and solubility parameter (δ).⁴

We have not used the χ parameter for the following reasons. The parameter is temperature-dependent,¹⁶ and the dependence may vary from one plasticizer to another. The method used to obtain the parameter for

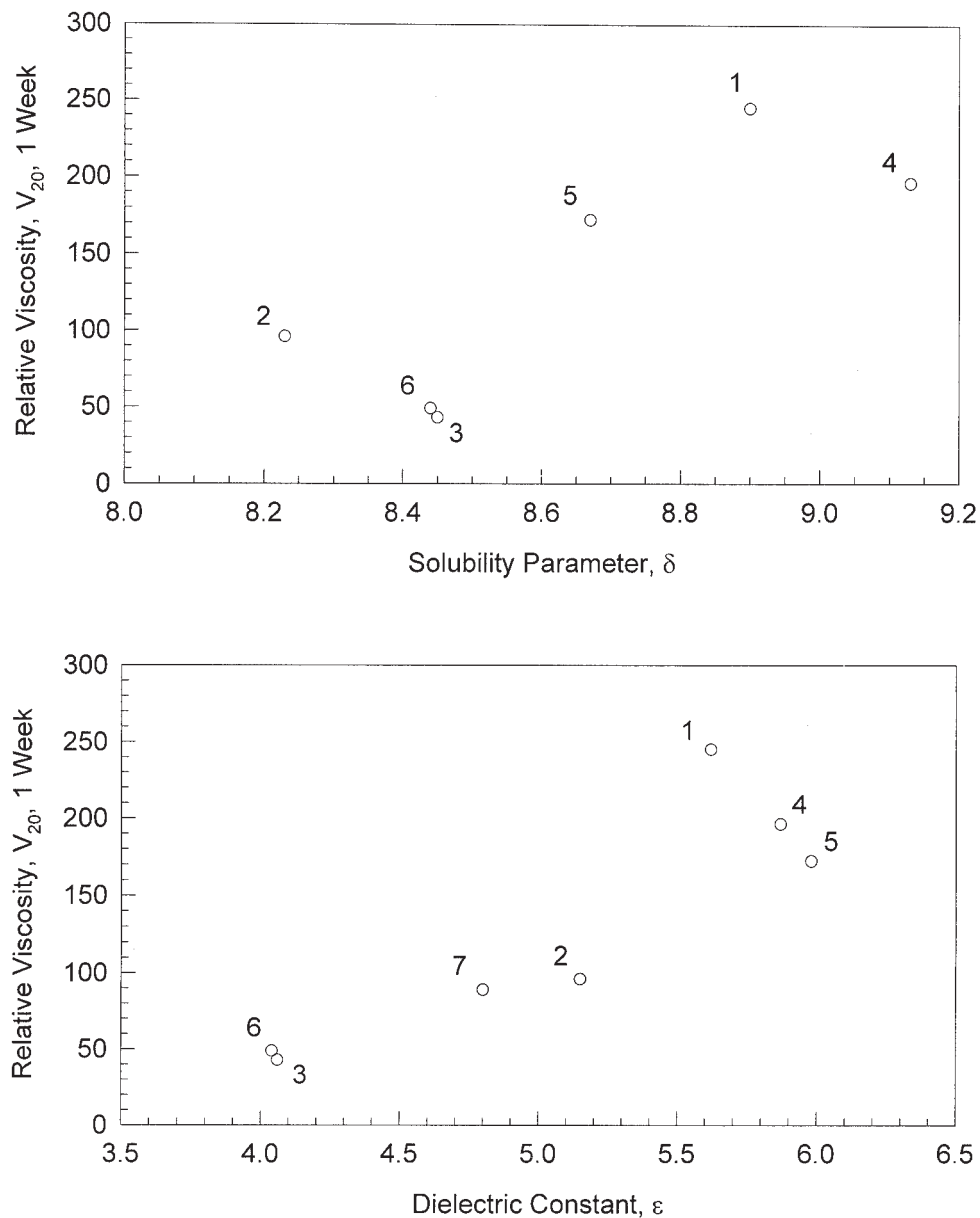


Figure 9 Viscosity after 1 week. It is not related to δ or ϵ of the plasticizer.

PVC-plasticizer interactions is a gel-sol transition temperature measurement,¹⁷ which is performed at high temperatures. This case requires a parameter at room temperature. Also, the gel-sol transition is dependent on the crystalline morphology of PVC, which is variable. Considerable variations in the viscoelastic properties of plastisols were observed in the temperature range of the gel-sol transition with 11 grades of PVC for plastisol applications.^{1,18} Therefore, it is preferable to use the physical parameters of the plasticizers themselves rather than the parameter of interaction between PVC and the plasticizers. The ϵ and δ data were taken from the literature⁴ and are listed in Table II.

Examples of the analysis are given with the viscosity of resin A at 1 week of aging. First, samples 1-6 are

examined; sample 7 is left for later discussion because there is some question on how to treat a polymeric plasticizer. Figure 9 shows that the 1-week viscosity data are related to neither δ nor ϵ . Not even a trend can be found. Figure 10 presents similar plots, except that the PVC-plasticizer interaction is assumed to depend on the physical parameter divided by the MW.¹⁹ However, our attempt to find a relationship failed.

Correcting the viscosity for the difference in ϕ

For practical reasons, these plastisol samples were formulated on a mass basis. However, the densities of the plasticizers were different. This made ϕ of the PVC particles of one plastisol different from another. With

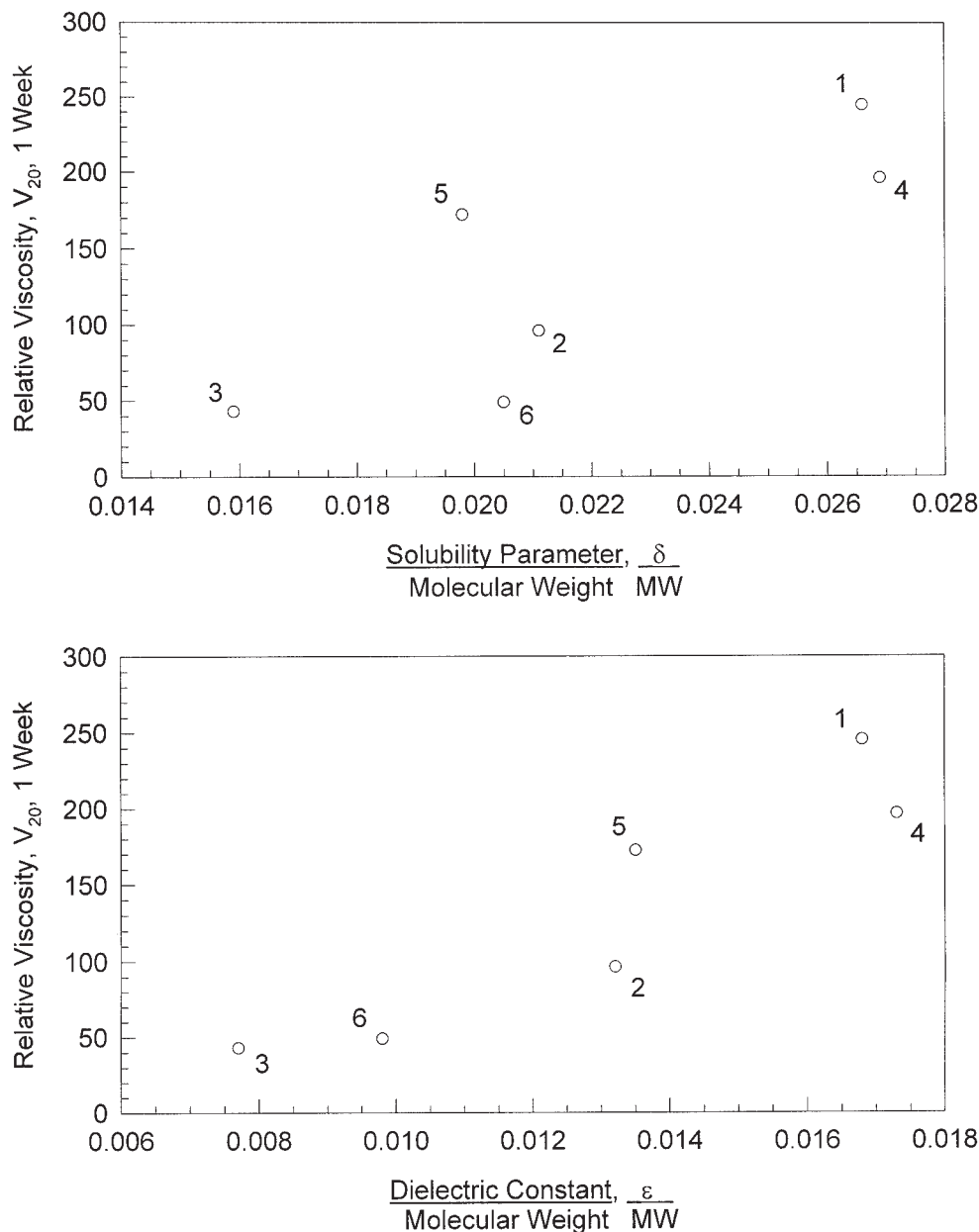


Figure 10 Viscosity after 1 week. It is not related to δ divided by MW or ϵ divided by MW of the plasticizer.

concentrated dispersions such as these samples, a small difference in ϕ can make a large difference in e_{gr} , because of a logarithmic relation: $\log \eta_r \propto \phi/\phi_c$ [eq. (1)].⁹ We use this relation for calculating the viscosity at the same value of ϕ (0.50) from the observed viscosity at different volume fractions. The data for this calculation are given in Table VI.

In the aforementioned calculation, the volume fraction of the liquid phase, $1 - \phi$, represents that of the plasticizer and stabilizers. The density of the plasticizer was that for the mixture of the plasticizer and stabilizers. Therefore, there were small systematic errors, which did not affect establishing the relationship between the parameters of the plasticizer and viscosity aging.

Figure 11 shows the calculated η_r values for $\phi = 0.50$ plotted against either δ or δ/MW . Apparently, there is no relation between η_r and δ . Although the plot of η_r versus δ/MW shows a trend for the phthalates (1–3), overall it does not establish a quantitative relationship.

Figure 12 shows a similar plot of η_r versus either ϵ or ϵ/MW . With the exception of sample 1, the data for η_r and ϵ appear to be related. On the other hand, in the plot of η_r versus ϵ/MW , the data for samples 1 and 4 deviate from the straight line. Which one of these relationships is applicable to this experiment must be examined.

Because the observed η_r values at various ϕ values were first converted to ϕ_c and then, with this ϕ_c value,

TABLE VI
Calculation of the Viscosity at a Constant Volume Fraction

Sample	Plasticizer	Observed				Calculated η_r ($\phi = 0.50$)
		η_r	ρ^a	ϕ	ϕ_c	
1	DHP	245	1.008	0.533	0.693	85
2	DEHP	96	0.982	0.525	0.722	54
3	DTDP	43	0.952	0.517	0.764	33
4	DEHP/S160 ^b		0.982			
			1.119			
5	blend	196	1.052	0.545	0.717	56
	DEHP/S148 ^c		0.982			
			1.070			
6	blend	172	1.028	0.537	0.711	60
	DOZ		0.915			
7	DEHP/G54 ^d	49	0.982	0.510	0.746	40
			1.100 ^e			
	blend	89	0.979	0.525	0.724	52

DHP = di-isohehexyl phthalate; DTDP = di-tridecyl phthalate; DOZ = di-octyl azelate.

^a The densities of the plasticizers were taken from ref. ⁴. The densities of the blends are given as the mass average.

^b Butyl benzyl phthalate.

^c Decyl diphenyl phosphate.

^d Poly(ethylene glycol sebacate).

^e Amorphous density.²⁰

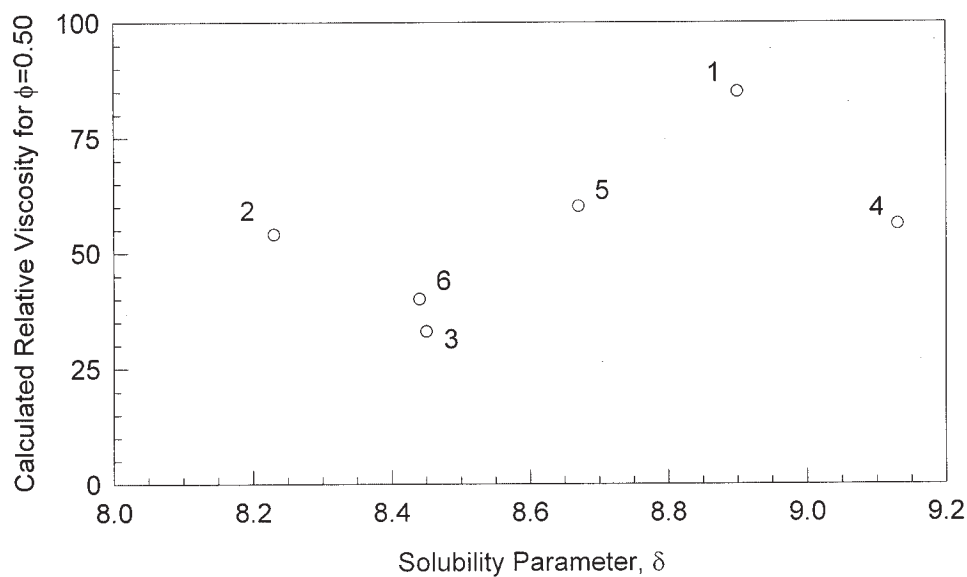
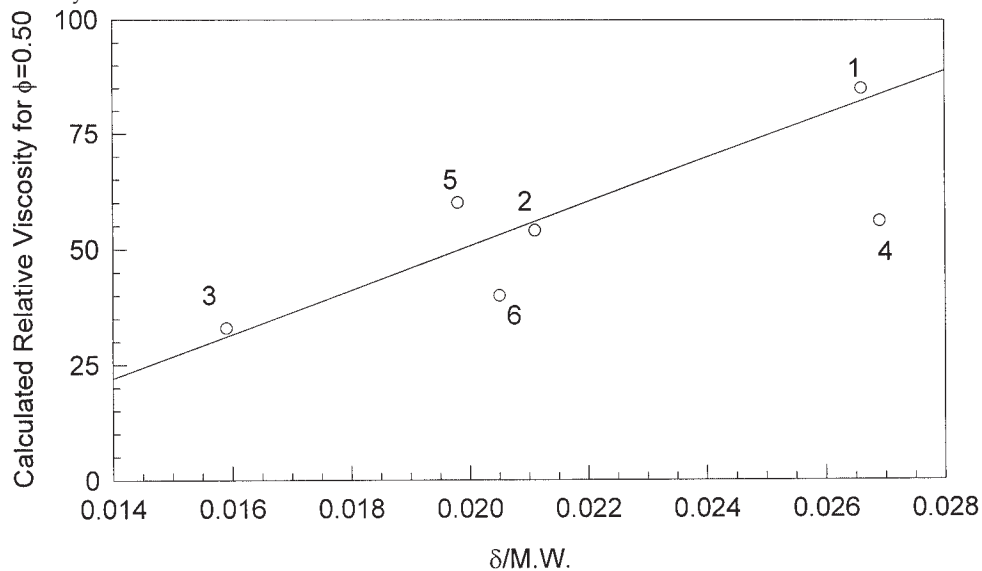


Figure 11 Viscosity after 1 week (calculated for a constant value of ϕ), It is not well related to δ or δ divided by MW.

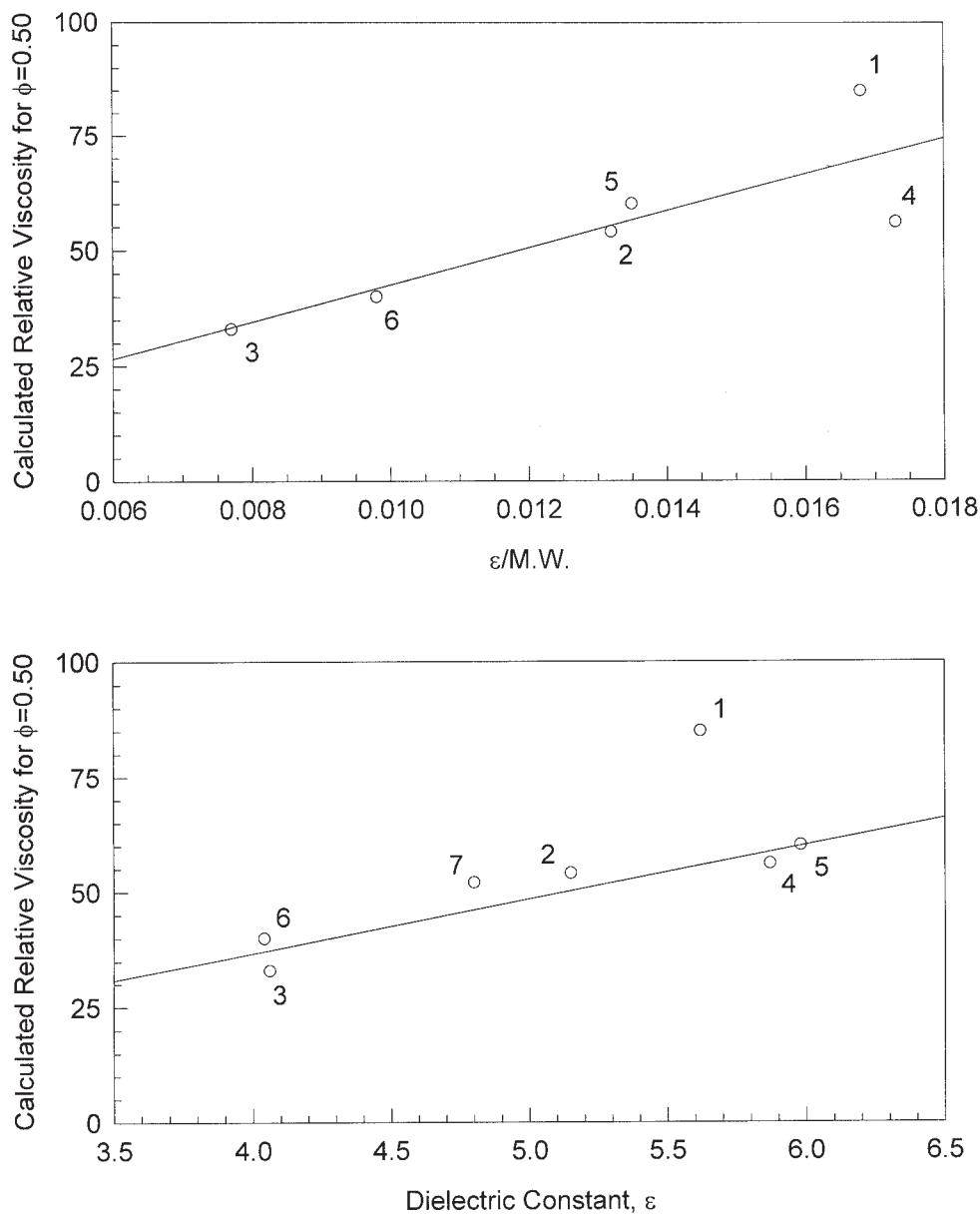


Figure 12 Viscosity after 1 week (calculated for a constant value of ϕ). It is related to ϵ or ϵ divided by MW (there are some exceptions).

η_r was calculated for a constant value of ϕ , the relationship of ϕ_c and ϵ or ϵ/MW must be examined first.

In Figure 13, no quantitative relation was found between ϕ_c and ϵ , except for samples 1, 2, 3, and 7. On the other hand, with the one exception of sample 4, a good relationship was found between ϕ_c and ϵ/MW . In light of the relationship of eq. (1), it is consistent to plot $\log \eta_r$ against ϵ/MW . A good relationship was obtained, as shown in Figure 14, with the exceptions of samples 4 and 7; this is consistent with what can be seen in Figure 13.

In this problem, the reduction of ϕ_c represents some deagglomeration, which results in a reduction of larger particles and an increase in smaller particles.

The larger values of ϵ/MW are more effective in promoting deagglomeration. Plasticizer 4 is not as effective in causing deagglomeration as might be expected from its ϵ/MW value. Its behavior is more like that of plasticizer 2, DEHP, which is one of the components of the blend in plasticizer 4. Butyl benzyl phthalate, the other component, has a value of ϵ much higher than that of DEHP, but the blend of the two is only as effective in promoting deagglomeration as DEHP alone. Whether this is the nature of this blend, in which DEHP preferentially attacks PVC, or the intrinsic nature of butyl benzyl phthalate must be examined.

The data in the literature²¹ indicate that butyl benzyl phthalate (BBP) alone and a mixture of DEHP and

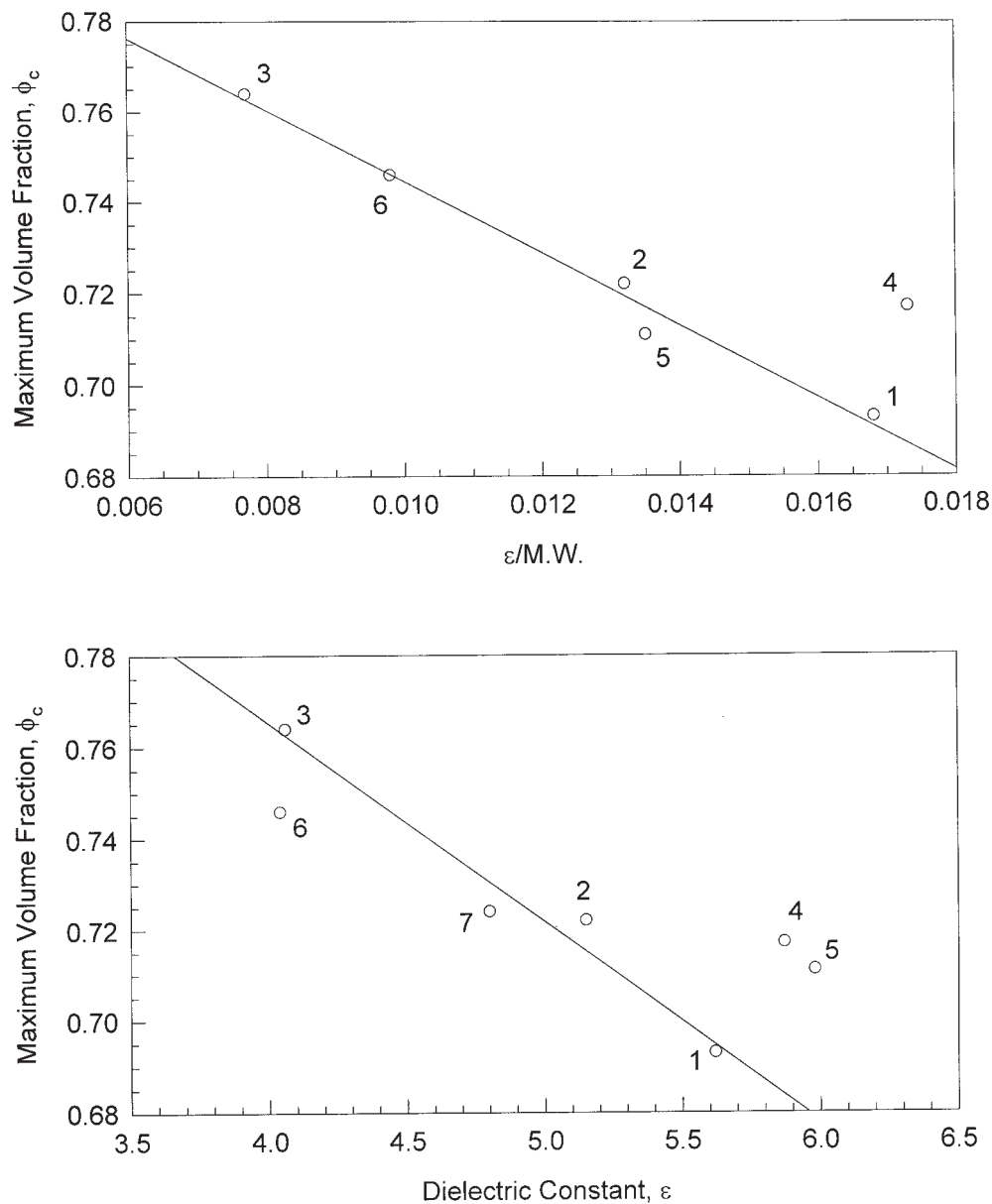


Figure 13 ϕ_c , a measure of deagglomeration. It is related to ϵ or ϵ divided by MW (there are some exceptions).

BBP are much more effective than DEHP alone in promoting viscosity aging. The data taken from the publication are given in Table VII.

With these data as a guide, the expected value of η_r for sample 4 was calculated from the data for sample 2 by multiplication with the ratio 2.32/1.27. In Figure 14, the calculated viscosity is plotted for sample 4'. This point lines up reasonably well with the data of the other samples. However, this does not give a satisfactory explanation for the apparent anomaly of sample 4. The PVC resin used in the literature was a different type that yielded a relatively small increase in the viscosity of the plastisol with time. The mechanism of viscosity aging for that resin-plasticizer system did not appear to be deagglomeration.

The ϵ/MW data for sample 7, which contained a polymeric plasticizer, was calculated in two ways: for one of them, $MW = 3420$ was used under the assumption that the whole molecule, as a unit, contributed to the deagglomeration. For the other calculation, the monomeric unit ($MW = 228$) containing two carboxyl groups was considered to be the unit. With the former assumption, the contribution of the polymeric plasticizer was almost negligible. However, as point 7 in Figure 14 shows, the use of $MW = 3420$ underestimated ϵ/MW , and this implied that the contribution of the polymeric plasticizer was not negligible. On the other hand, the use of the monomeric MW resulted in an overestimate of ϵ/MW (point 7' in Fig. 14).

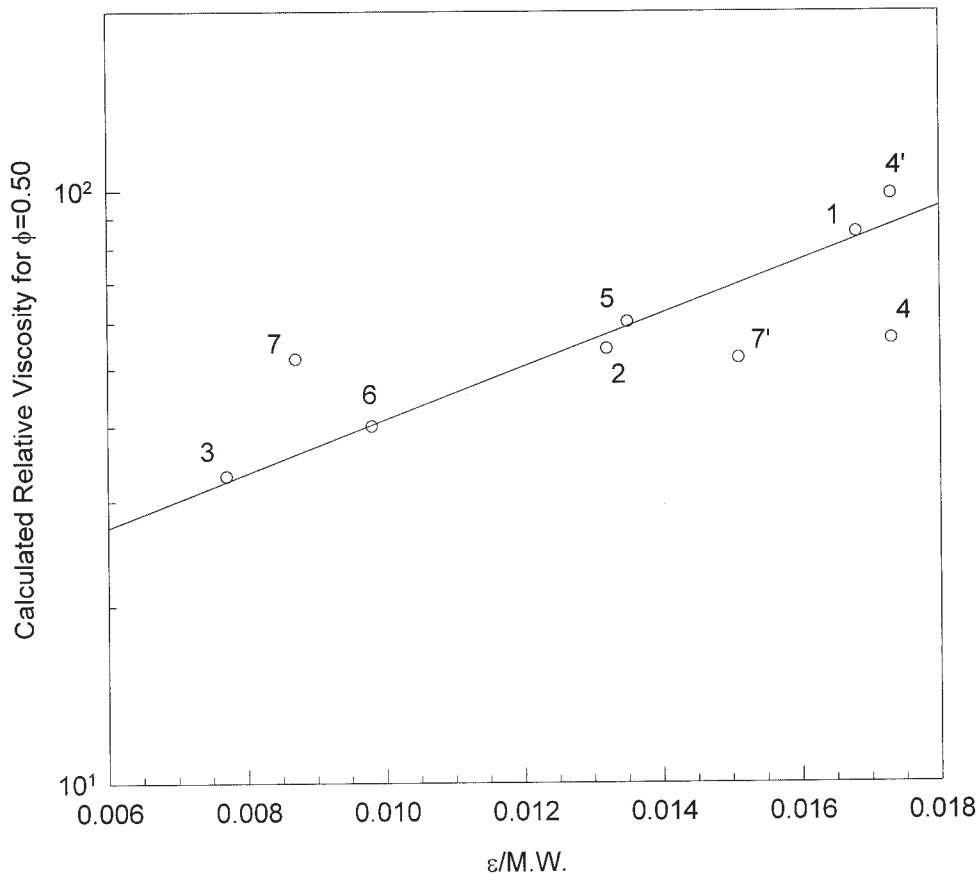


Figure 14 Viscosities of Figure 12, in a logarithmic form, plotted against ϵ divided by MW.

Both samples 4 and 7 contained plasticizer blends, for which it was difficult to establish a quantitative relationship between the viscosity aging and the physical parameters of the plasticizers. In both blends, DEHP may have a dominant effect on deagglomeration.

The same conclusions were reached with the data for resin B, as might have been expected from the relationship shown in Figure 7.

CONCLUSIONS

The causes of viscosity aging may be different for different grades of PVC resins, which are manufactured to meet different processing requirements. With one resin containing friable agglomerates, the predominant mechanism of the viscosity aging was

deagglomeration. With the other resin containing non-friable agglomerates, a few percent of ultrafine particles, consisting of low-molecular-weight polymer and dissolving in the plasticizer, caused a noticeable increase in the viscosity.

In general, PVC resins, manufactured for plastisol applications, contain emulsifiers, which are used for polymerization but are not removed before drying. The emulsifier influences the viscosity aging in the beginning but has no specific effect on the viscosity at 1 week of aging. The emulsifier appears to be extracted before 1 week is reached.

A quantitative relation between the viscosity aging and the physical properties of the plasticizers must be examined at a constant volume fraction. If the formulation is weight-based, the data must be converted into one that is volume-based because plasticizers have variable densities and a small difference in ϕ produces a large difference in the viscosity.

With four plasticizers and one plasticizer blend, the 1-week viscosity was quantitatively related to ϵ divided by MW of the plasticizer. ϵ may be regarded, in this case, as representing the ability of a plasticizer to cleave contacts between particles of PVC, thus enhancing the deagglomeration.

TABLE VII
Viscosity Aging Data from the Literature²¹

Plasticizer	Parts per hundred parts of resin by weight	Viscosity increase 1 week/initial
DEHP	60	1.27
BBP	60	2.58
DEHP/BBP	30/30	2.32

For samples containing blended plasticizers, the mass-average value of ε/MW was used in the correlation. One sample with blended plasticizers (DEHP and BBP) did not fit the previously established relationship. It acted as if the plasticizers were DEHP alone, and a higher value of ε/MW of BBP did not have any effect. Whether this was because DEHP in the blend preferentially attacked PVC or not must be examined. Likewise, a blend of DEHP and a polymeric plasticizer did not match the previously established relationship. A question remains as to how to calculate ε/MW or find other suitable parameters for the polymeric plasticizer.

No quantitative relationship was found between the viscosity aging and δ of the plasticizer.

The experimental data were obtained by D. W. Ward.

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