

Rheology of Poly(vinyl chloride) Plastisol for Superhigh Shear-Rate Processing. I

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ABSTRACT: In coating operations with poly(vinyl chloride) plastisol, there is a high shear limit because the flow becomes unstable. However, there is an indication that the flow becomes stable at superhigh shear rates well past the unstable region. This article explores the effect of the particle size (with a similar size distribution spread) and the effect of the amount of the emulsifier on the flow at superhigh shear rates. It has been known that below the flow instability, larger particles lead to a lower

viscosity, and an increased amount of the emulsifier leads to a higher viscosity. The question is whether or not the same trends persist at superhigh shear rates. Observations in this study confirm these trends. In addition, the emulsifier has been found to enhance the interparticle attraction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3605–3609, 2010

Key words: poly(vinyl chloride) (PVC); rheology; plastisol

INTRODUCTION

A major application of poly(vinyl chloride) (PVC) plastisol is coating; the coating speed varies, depending on the given process and the shapes of the products. The coating of flat surfaces, such as paper and cloth coating, is performed at high speeds. Because of the high speeds and the thinness of the coatings, the flow is under high shear rates. However, there is a limit to the useful shear rate range because the flow becomes unstable. In coating operations, films become nonuniform and even torn.

In a previous publication,¹ we suggested that beyond the flow instability, there is a stable flow region at superhigh shear rates. This article is the first of a series examining the flow at superhigh shear rates. First, two problems are treated: the effect of the particle size and the interparticle interaction. In one of our earlier publications,² we reported that the presence of larger particles in a composition consisting of smaller particles produced a significant reduction in the viscosity at shear rates below the instability. In this study, we examined two samples that had similar particle size distributions but varied in the overall particle size. We already knew that a sample with larger particles has a lower viscosity at shear rates below the instability.² We needed to

determine whether or not the same is true at shear rates above the instability.

In addition to the steady-state viscosity measurements, dynamic measurements³ were performed to complement the former results.

To examine the effect of the interparticle interaction, two plastisol samples with different amounts of an emulsifier were prepared. The steady-state flow data were analyzed with respect to the stress-induced phase separation⁴ and the cohesive strength of the immobilized layer.⁵

EXPERIMENTAL

Samples

The sample PVC resins were all type 124A⁶ and were supplied by PolyOne Corp. (Avon Lake, OH). They were made under the same polymerization conditions and with the same posttreatment (drying condition). The minor modifications made for the purpose of this investigation are listed in Table I, and the plastisol formulation is given in Table II.

The particle size distributions of the samples are shown in Figure 1, in which the cumulative mass is plotted against the particle size from smaller particles to larger particles.

The distributions of samples 94 and 96 were very similar, as they were intended to be. The spread of the particle size distribution of sample 98 was very similar to the spread of the other two samples, but the actual particles were almost twice as large.

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TABLE I
Sample Identification

Sample	Description	Amount of the emulsifier
94	Control	Standard
96	Modified to contain more emulsifier	1.14 × standard
98	Modified to have a larger particle size	Standard

The plastisols were aged for 2 days to stabilize the initial increase in the viscosity.⁶

Instruments

A Rheometric (TA Instruments, New Castle, DE) model RDSII mechanical spectrometer was used with a coaxial cylinder in both steady-state and dynamic modes at 27°C. The steady-state measurements were performed at shear rates ranging from 10^{-1} to 3×10^2 s⁻¹.

The dynamic measurements were performed in the angular frequency range of 10^{-1} to 10^2 rad/s. The strain amplitude was varied from 2 to 1024%.

The superhigh shear rate data were obtained with a Sieglaff-McKelvey (Tinius-Olsen Testing Machine, Co., Wallingford, CT) controlled-stress capillary rheometer with a capillary with a length-to-diameter ratio of 49.8. No correction was made for the entrance loss because preliminary experiments showed that the loss was negligible in comparison with the flow resistance across the capillary. The shear rates ranged from 500 to 4000 s⁻¹, at which the flow was stable. No corrections were made to convert the observed apparent values of the shear stress and shear rate to the absolute values because the apparent values of the viscosity were adequate for comparing the three samples.

RESULTS

The steady-state viscosities are plotted against the shear rates in Figure 2. The concentric cylinder data show pseudoplastic flow at low to intermediate shear rates and dilatant flow at high shear rates. In the dilatant region, there is a sharp rise in the negative normal stress that suddenly drops because of the instability.⁷ The capillary flow data match the

TABLE II
Plastisol Formulation

	phr by weight
PVC	100
Diisononyl phthalate	57
Epoxidized soybean oil	3
Thermocheck 120 LOHF (stabilizer)	2

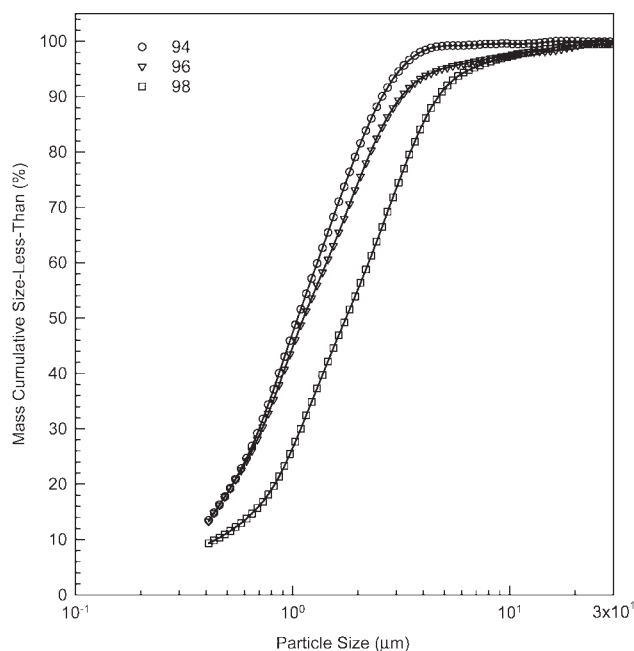


Figure 1 Cumulative mass distribution of the particle size in the plastisols.

cylinder data reasonably well, although there are no overlaps. Actually, the capillary data show the instability at shear rates below those shown in the figure. The instability is indicated by the widely scattered values of the observed viscosity. We shall discuss the instability in a forthcoming article in more detail. The capillary data shown here are only in the stable flow regions. Our earlier expectation¹ is correct:

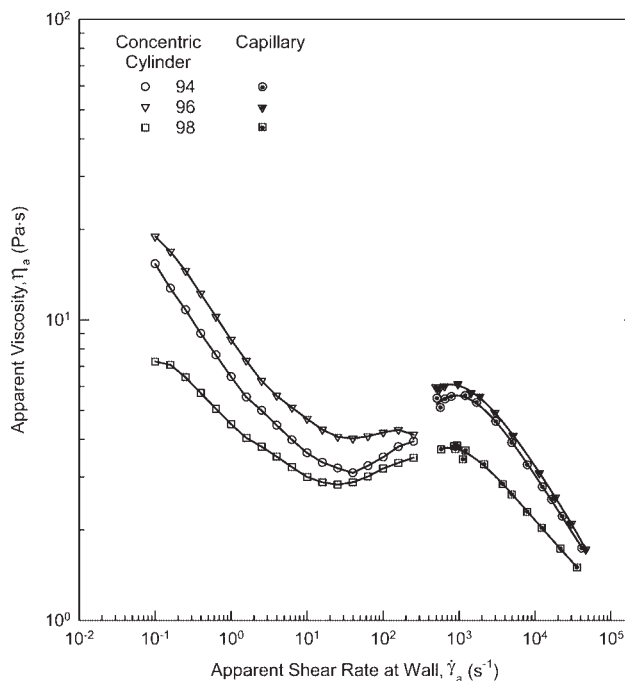


Figure 2 Steady-state viscosities below and above the instability.

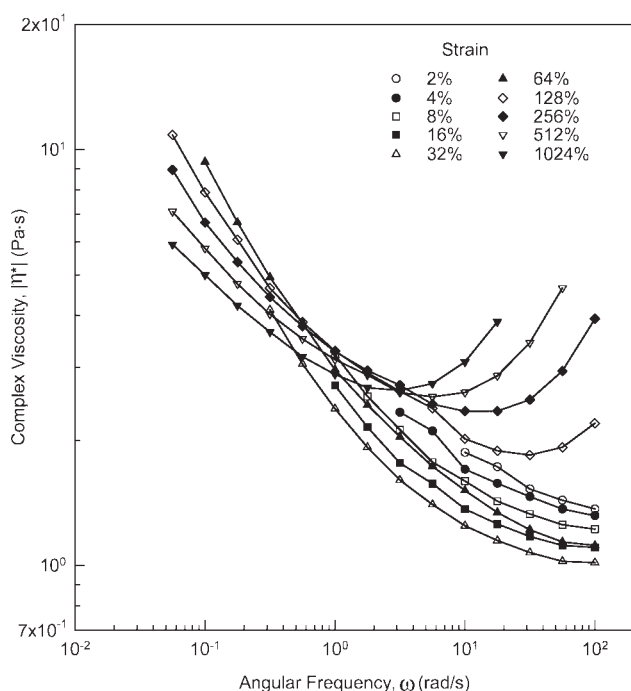


Figure 3 Absolute values of the complex viscosity at different strain amplitude levels for plastisol sample 94.

beyond the instability, there is a stable flow region at superhigh shear rates. The viscosity displays a maximum and then decreases with the increase in the shear rate.

The effect of the particle size on the viscosity is significant, even though the pattern of the size distribution is similar. Larger particles (sample 98) pro-

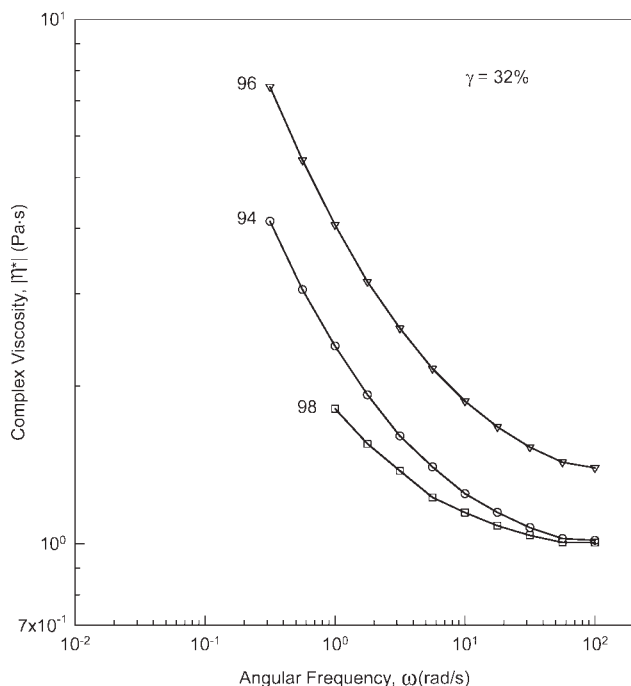


Figure 4 Complex viscosities at a strain amplitude of 32%.

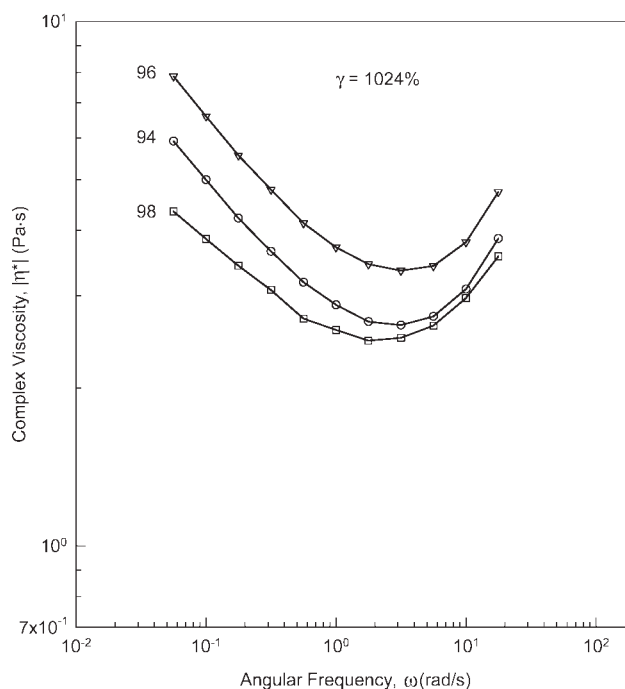


Figure 5 Complex viscosities at a strain amplitude of 1024%.

duce a lower viscosity than control particles (sample 94). This must be because with a larger particle sample, the interparticle distance is larger and the total surface area is smaller in comparison with a smaller particle sample.

A larger amount of the emulsifier has a decisive effect on the viscosity, even though the difference in the amount of the emulsifier is only 14%. This fact implies that the emulsifier influences the interparticle interaction. The nature of the interaction is discussed later.

The dynamic data for sample 94 are shown in Figure 3 as the absolute values of the complex viscosity versus the frequency. The level of the high-frequency viscosity curve becomes lower as the strain amplitude increases from 2 to 32% and then, in a reversal, increases with increasing strain amplitude, as observed before.³

The curves of three samples are shown at the strain amplitude of 32% in Figure 4 and at the strain amplitude of 1024% in Figure 5. The observed data at 32% show pseudoplastic flow, which reaches the viscosity minimum. At 1024%, the curves include pseudoplastic flow, the viscosity minimum, and dilatant behavior.

The effects of the particle size and the interparticle interaction are the same as those discussed for the steady-state data. The only exception is that the effect of the particle size diminishes as the frequency increases, whereas the effect persists as the shear rate increases in the steady-state flow. At this time, we do not have an explanation for this observation.

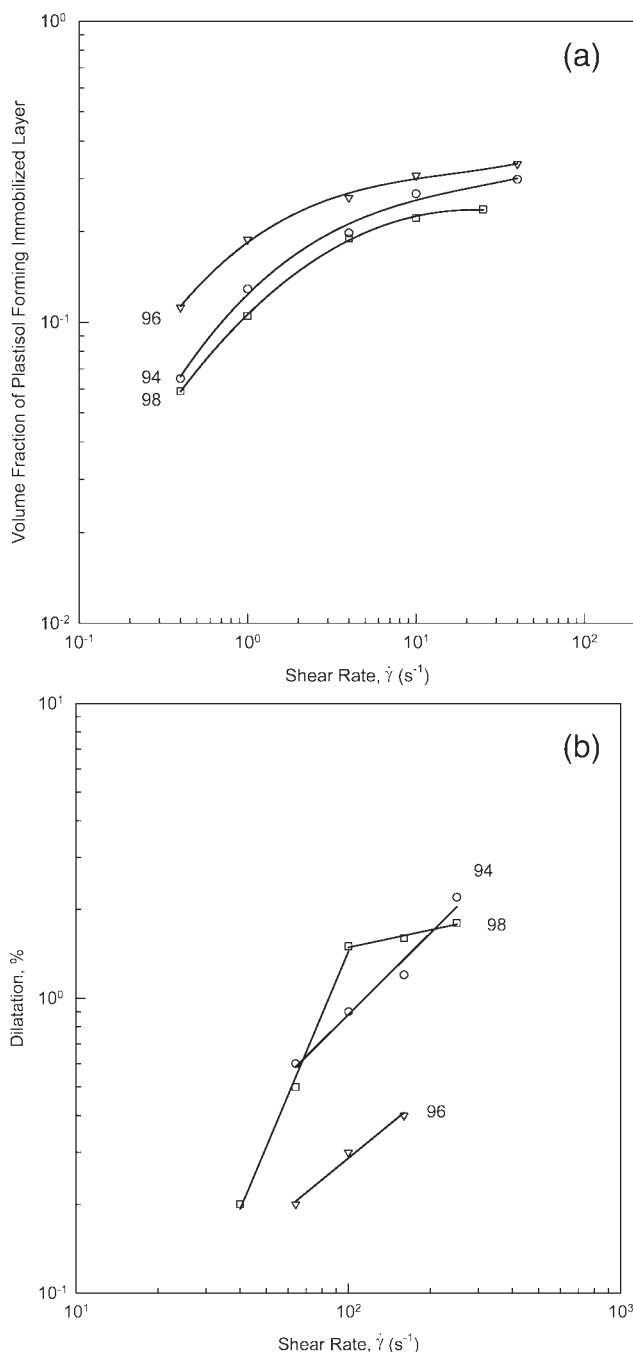


Figure 6 (a) Buildup of the immobilized layer in the pseudoplastic region and (b) dilatation of the immobilized layer in the dilatant region.

DISCUSSION

Figure 6(a,b) shows the buildup of the immobilized layer in the pseudoplastic flow region and the percent dilatation in the dilatant region in the steady-state flow. For the former, the method of calculation is given in ref. 4, and for the latter, the method of calculation is given in ref. 5.

The effect of the particle size on the buildup of the immobilized layer is rather small, sample 98

showing slightly smaller buildup than sample 94. Therefore, sample 98 had a significantly lower apparent viscosity than sample 94 (Fig. 1) because of the difference in the viscosity in the mobile (flowing) phase. Sample 96 showed a larger degree of buildup of the immobilized layer in comparison with the other samples, and this indicates the presence of the interparticle attractive force.

The extents of dilatation of samples 94 and 98 were about the same, although the trend was not exactly the same. Sample 96 dilated much less in comparison with the other samples, and this indicates that the interparticle attraction holds particles together against the dilating force.

Through analyses of dynamic data, the properties of the immobilized layer were elucidated, as shown in Table III. The frequency was chosen to be 10 rad/s for two reasons: the observation covered the widest range of strain amplitudes, and the largest differences were seen among the samples. The strain amplitudes were 32 and 1024%.

With reference to the data at the amplitude of 32%, the packing density of the immobilized layer was evaluated according to a previously described method⁵ from the flow behavior at a low frequency (10⁻¹ rad/s) and with the strain amplitude extrapolated to zero. The values remain the same at the strain amplitude of 32% and the frequency of 10 rad/s because the dilatation has not yet started. The higher value indicates tighter packing. The larger particles give somewhat tighter packing (sample 98 vs sample 94). Whether or not the difference is within the experimental error is not known. A larger amount of the emulsifier seems to produce looser packing (sample 96 versus sample 94) and leads to a higher viscosity. This may be an artifact, resulting from the thicker surface coverage with a larger amount of the emulsifier, which makes the actual particle concentration higher than what is given in Table II. An alternate explanation is that the particles in PVC plastisol tend to form chains,⁸ instead of neatly fitting in a given volume. The chain formation leads to looser packing, and the tendency is enhanced by the stronger attractive force between particles (i.e., a larger amount of the emulsifier).

TABLE III
Packing Density and Dilatation of the Immobilized Layer

	Sample	Packing density	Dilatation (%)
Strain amplitude of 32% and frequency of 10 rad/s	94	0.69	0
	96	0.67	0
	98	0.71	0
Strain amplitude of 1024% and frequency of 10 rad/s	94	0.64	8
	96	0.63	6
	98	0.65	9

The packing densities at the amplitude of 1024% are lower than those at 32% because the immobilized layers are dilated. A comparison of the values of three samples shows the same trend found at the amplitude of 32%. However, the differences are much smaller. The immobilized layer of sample 96 dilated somewhat less than those of the other two samples. This indicates that a larger amount of the emulsifier provides a stronger attractive force.

CONCLUSIONS

Within the particle size range of our investigation, larger particles produce a lower viscosity when the size distributions are similar. A larger amount of the emulsifier leads to a higher viscosity. These trends persist both below and above the instability region.

The emulsifier was found to enhance interparticle attraction.

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