

# Absorption of Trioctyl Trimellitate into Mass-Polymerization and Suspension-Polymerization Poly(vinyl chloride)

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**ABSTRACT:** Poly(vinyl chloride) (PVC) slush powder has been widely used; we prepared it by dry blending. We found that the absorption of plasticizer by the PVC resins was the most important factor in the dry-blending process and, further, that different types of PVC resin had different absorption rates. This results of this study provide new information about the relationship of absorption to PVC and other parameters. Haake rheomix testing and the quantity of plasticizers absorbed by the PVC resins were used to characterize the absorption process. Suspension-polymerization poly(vinyl chloride) (SPVC) and mass-polymerization poly(vinyl chloride) (MPVC) in different sizes were used for the test. The results showed that the MPVC absorbed the plasticizer more quickly than SPVC, especially at a higher temperature. However, for the same PVC resin type, the absorb-

ing speeds were nearly independent of particle size. The studies that used a scanning electric microscope and specific surface area revealed that the morphology of the two types of particles was different. The surfaces of the individual particles of SPVC were smoother than those of MPVC. There was a "skin" covering the SPVC particles, whereas with the MPVC particles, the primary polymer was exposed directly on the surface. This difference in morphology was shown to be a significant factor in the different rates of absorption of the plasticizers for the different PVC resins. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2369–2374, 2004

**Key words:** poly(vinyl chloride) (PVC); morphology; rheology; blending

## INTRODUCTION

In the early days of rotational molding, poly(vinyl chloride) (PVC) plastisols were used to make some toys. At the beginning of 1990s, some patents were related to the use of free-flowing powdered PVC compounds,<sup>1,2</sup> which are widely used for many product types today. Compared with PVC plastisols, powdered PVC compounds has the following advantages:<sup>3</sup> when the powdered PVC compounds are stored, the form and the performance do not change for a certain period, usually more than 1 year. So it is very convenient for packaging and transportation, whereas PVC plastisols are not stable for even 3 months; Also, when powdered PVC compounds and PVC plastisols are used in slush molding, the thickness of the products made from powder is more uniform than with plastisols.

However, compared with PVC plastisols, the preparation process of powdered PVC is more complex because a lot of plasticizers must be used to obtain a soft product. That is, PVC resins must absorb a great quantity of plasticizer to produce a powdered blend.

Therefore, the process of absorbing plasticizers by PVC resins dominates the preparation process. To produce high stability in the product, the plasticizer is usually a special type, for example, a complex structure plasticizer such as trioctyl trimellitate (TOTM). Although some researchers have worked on PVC absorption plasticizers,<sup>4</sup> they have seldom reported the processing of PVC resins with TOTM or discussed the absorption of TOTM, whose viscosity is higher than that of di-(2-ethylhexyl) phthalate (DOP) and diisononyl phthalate (DINP). Also, when we prepared the PVC powdered blend, the temperature was more than 100°C; so it was necessary to study the behavior of the PVC resin absorption of TOTM at different temperatures. In this study, we examined the different behaviors of mass-polymerization poly(vinyl chloride) (MPVC) and suspension-polymerization poly(vinyl chloride) resins and their absorptions of TOTM.

## EXPERIMENTAL

### Materials

Two types of commercial PVC resins were used in dry blending, MPVC and SPVC, and the DP value of each resin was 66. On the basis of the two PVC resins, eight samples were used. The samples' reference and the type of resins are shown in Table I.

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TABLE I  
Sample References and the Types of Resins

Reference	Sample size
MPVC	MPVC, nonsifted
SPVC	SPVC, nonsifted
M-2	MPVC, passed sieve no. 100, did not pass sieve no. 120
M-3	MPVC, passed sieve no. 120, did not pass sieve no. 140
S-1	SPVC, passed sieve no. 80, did not pass sieve no. 100
S-2	SPVC, passed sieve no. 100, did not pass sieve no. 120
S-3	SPVC, passed sieve no. 120, did not pass sieve no. 140
S-4	SPVC, passed sieve no. 140

The plasticizers were DINP and TOTM. A Ca-Zn type stabilizer and Irganox 1010 were also used in the recipes.

### Methods

The Haake rheomix test was used to characterize the absorption of plasticizers by the PVC resins. The stabilizers, costabilizers, and antioxidants were mixed with the PVC resin first; then at same time, the mixture and plasticizers were added to a Haake rheomix (Haake Polylab System, Karlsruhe, Germany), which was heated to a certain temperature, for example, 110°C; the speed used was 30 rpm.

The recipe use for the Haake rheomix test is given in Table II.

The quantity of the absorption of plasticizers by the PVC resins was also measured, in accordance with ISO 4608-84.

The morphology of the PVC resin particles was studied by scanning electron microscopy (SEM).

TABLE II  
Haake Rheomix Test Recipe

Component	Weight ratio (phr)
Plasticizer	70
Ca-Zn stabilizer	8
Irganox 1010	1

## RESULTS AND DISCUSSION

### Haake rheomix test

When preparing the slush powder, we found that the speed of absorption of the plasticizers by the PVC resins was an important characteristic, which influenced the whole process.<sup>5</sup> However, it was difficult to measure this in the process of dry blending in the high-speed mixer. In the experiment, the Haake rheomix was used to test absorption; the curves of torque versus time were recorded, and from these curves, the speed of absorption of plasticizers at the blending temperature were characterized.

Figure 1(a,b) shows the difference in absorption between SPVC and MPVC at 120 and 110°C. As shown in Figure 1, because of the lower temperature of the PVC powder and plasticizer when they were added into mixer, the temperature curve decreased at the beginning; as the process continued, the temperature rose. At the beginning of the blending process, because the plasticizers had not yet been absorbed by the PVC resin, they acted as lubricants, which caused the torque to be lower. As the process continued, more and more plasticizer was absorbed by the PVC resin, which caused the torque to increase. When the plasticizers were absorbed completely, the torque reached its maximum. So, on the basis of the time required for the curve to reach its maximum, the speed of absorption of the plasticizers was compared. Table III lists the times obtained from Figure 1.

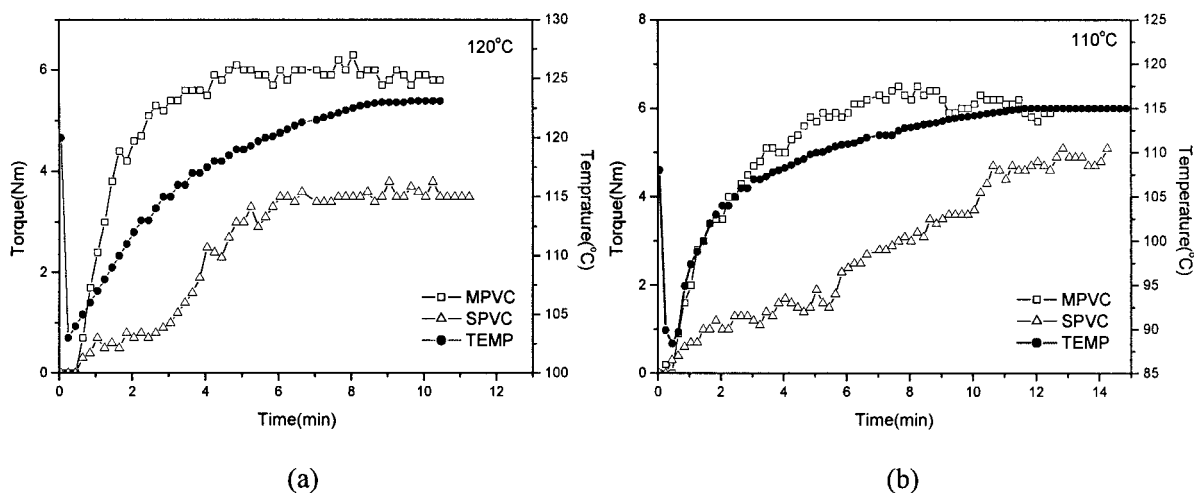


Figure 1 Results of the Haake rheomix test of MPVC and SPVC at (a) 120 and (b) 110°C.

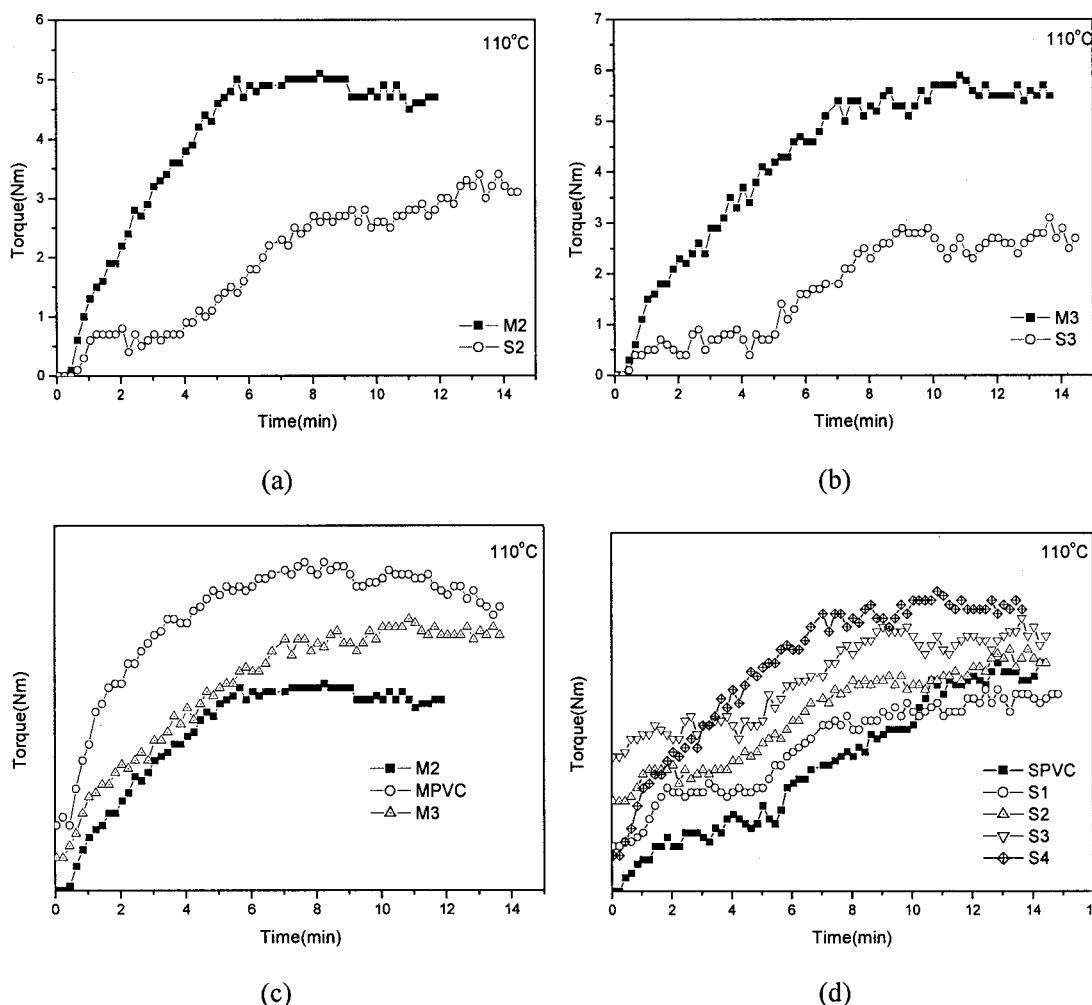
**TABLE III**  
Times Required to Reach Maximum Torque (min) for the Resins

Blend temperature (°C)	MPVC	SPVC
110	8.0	12.0
120	4.5	6.5

From Table III, it can be seen that the time required for the curve to reach its maximum torque for MPVC was significantly shorter than for SPVC at the different temperatures, which means the speed of absorption of plasticizer for MPVC was faster than that for SPVC. When the temperature increased, the speed of absorption of the plasticizers by the two PVC resins became faster, which was consistent with the results of the dry blend of PVC slush powder in the high-speed mixer. So selection of MPVC yielded higher product efficiency.

In our previous work, we found that the particle size distribution of MPVC was not the same as that of SPVC;<sup>6</sup> so we sieved SPVC and MPVC through several types of sieves (shown in Table I). Then, HAAKE rheomix tests were carried out with these PVC resins. The results are shown in Figure 2.

As shown in Table I, the sizes of M2 and S2 and M3 and S3 were almost the same. Figure 2(a,b) shows the results of the Haake rheomix test of these resins, which showed the same trend in both Figures 1(a) and 1(b). From Figures 1 and 2, it is obvious that absorption times of MPVC, M2, and M3 were about 6 min, and the absorption times of SPVC, S1, S2, S3, and S4 were also almost the same, about 9 min. In other words, although the particle size and size distribution of MPVC, M2, and M3 were different, the speeds of plasticizer absorption were the same; the same results were obtained for SPVC, S1, S2, S3, and S4. That is, the particle size and size distribution of the PVC resins were not the reasons for the different behaviors of plasticizer absorption.



**Figure 2** Results of the Haake rheomix test at 110°C: (a) M2 and S2; (b) M3 and S3; (c) MPVC, M2, and M3; and (d) SPVC, S1, S2, S3, and S4.

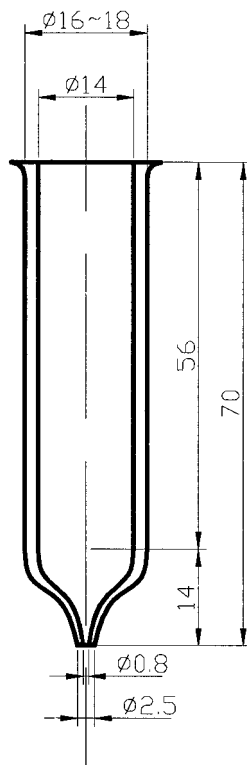


Figure 3 Shape and size of the centrifugal tube.

#### Quantities of plasticizer absorption by the PVC resins

The quantities of plasticizer absorption by the PVC resins were measured in accordance with ISO 4608-84. A specific centrifugal tube was used, whose shape and size are shown as Figure 3.

The process for measuring the quantities of plasticizer absorption by the PVC resins was as follows:

first, the tube was weighed, and  $0.100 \pm 0.002$  g of absorbent cotton was added in the tube and packed firmly. Then,  $2.0 \pm 0.5$  g of PVC resin and 4 mL of plasticizer were added into the tube one by one. After the tube was in place for 10 min, the mixture was separated by a centrifugal machine for 60 min at a rotation speed of 3000 rpm. Finally, the tube with cotton and PVC resin was weighed again. The absorption of plasticizer by absorbent cotton was measured with the same method. Then, the quantities ( $m$ ) of plasticizer absorption per 100 g of PVC resin was calculated with the following equation:

$$m = 100 \times \frac{m_3 - m_0 - m_2}{m_2 - m_1}$$

where  $m_0$  is the quantity of plasticizer absorption by the absorbent cotton,  $m_1$  is the weight of the tube with the absorbent cotton,  $m_2$  is the weight of the tube with the absorbent cotton and PVC resin, and  $m_3$  is the weight of the tube with the absorbent cotton and PVC resin after the absorption experiment.

If the experimental temperature was higher than the ambient temperature, the tube, plasticizer, and resins used in experiment were heated to the experimental temperature for more than half an hour.

Four types of PVC resin (MPVC, SPVC, M3, and S3) were used in the experiment. The results are shown in Figure 4.

As shown in Figure 4, at lower temperatures, for example, 20, 50, or 70°C, the quantity of the absorption of plasticizers by MPVC was a little bit higher than that by SPVC, and for each sample, the quantity of the absorption of plasticizers was almost same at different temperatures. With the temperature further increased,

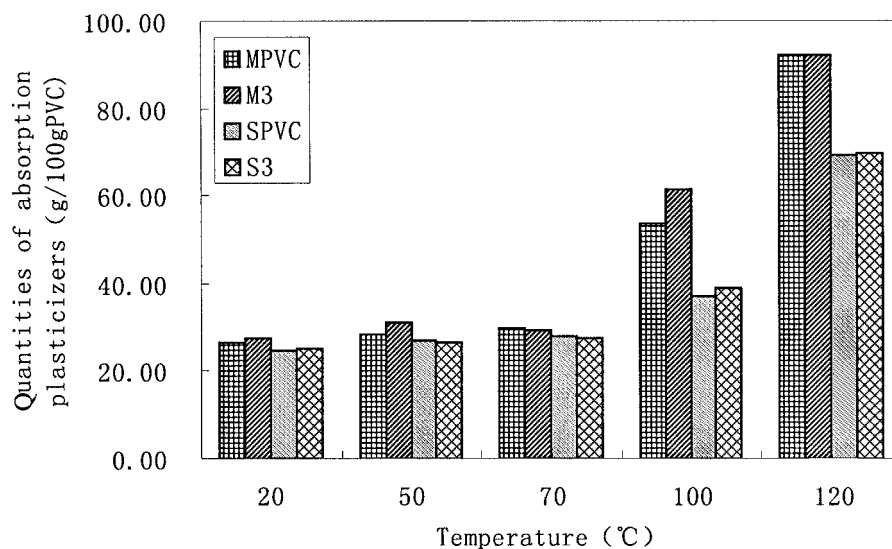


Figure 4 The quantities of absorption plasticizers of PVC resins.

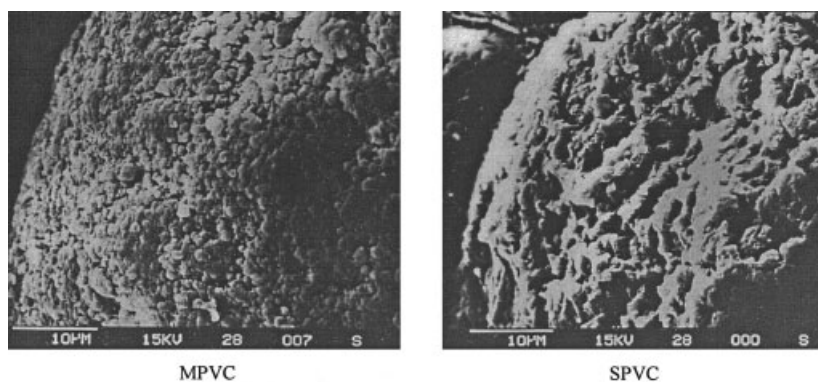


Figure 5 Scanning electron micrographs of MPVC and SPVC.

for example, up to 100°C, the quantity of absorption of each sample increased significantly, and the quantity of the absorption of plasticizers by MPVC resins was much more than that by SPVC resins.

#### Absorption behavior

It was easy to show that the absorption of plasticizer by PVC resins was strongly influenced by the type of PVC resin, whereas the absorption was almost independent of the particle size and size distribution. To explain this phenomenon, it was necessary for us to study the morphology of the two particles.

Figure 5 is the scanning electron micrographs of MPVC and SPVC. As shown in Figure 5, there were some grooves on the surface of the SPVC particles, the surface between the grooves was smooth, and the boundary of the SPVC particles was clear, as if a "skin" covered the SPVC particles. However, in contrast, there were many little balls on the surface of MPVC resin particles, and the boundary of the MPVC was ambiguous. As we know, the PVC particles are composed of a lot of primary particles with diameters of about 0.5–1.5  $\mu\text{m}$ , almost the same size as that of the balls, which means that many primary particles were directly exposed on the surface of the MPVC particles. As the result, when the plasticizers were added to SPVC and MPVC, the plasticizer entered more easily into the MPVC particles, which caused the MPVC to absorb the plasticizers more quickly than the SPVC. For the same reason, the MPVC absorbed much more plasticizer than did SPVC. At higher temperatures,

because the movement of the plasticizers and PVC molecules was faster, the differences in absorption behavior between the two PVC types became more obvious.

The values of the specific surface area of two types of PVC (shown in Table IV) also proved that the surface of SPVC was smoother than that of MPVC.

Table IV shows that the specific surface area of M3 was more than that of S3, although the particle sizes of M3 and S3 were the same, which meant that the surface of the MPVC resin was rougher than that of SPVC resin.

The following experiment further proved the function of the skin on the surface of the SPVC particles. The PVC particles were mixed with a specific type of acrylic glue, which could cure quickly at room temperature and become very hard. The mixture was poured into a rectangular mold, about 40  $\times$  6  $\times$  3 mm. After the glue cured, the specimen was broken, which resulted in the fracture of PVC particles, and the section photo was then studied by SEM (see Fig. 6).

As shown in Figure 6, there was a white band around the MPVC particles, although there was no band around the SPVC particles. These phenomena indicated that there existed a skin around the SPVC, which prevented the glue from entering these particles. The boundary between the SPVC and the glue was very clear. Because the primary particles were directly exposed on the surface of the MPVC particles, it was possible for the glue to enter the MPVC, which led to the white belt between the MPVC and the glue.

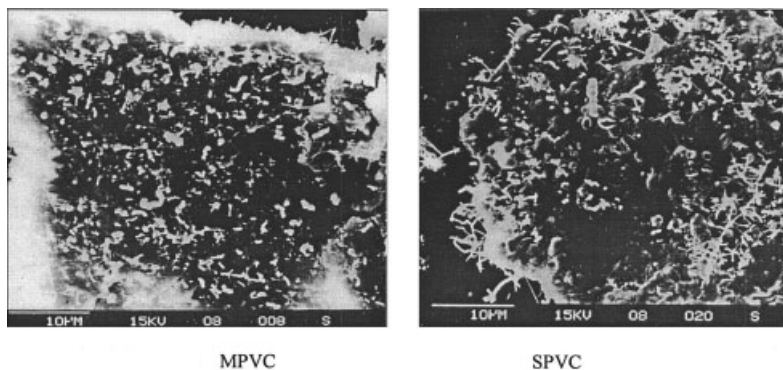
#### CONCLUSIONS

The general conclusions that we drew from this study are the following:

1. MPVC and SPVC could both be used to prepare slush powder. The speed of plasticizer absorption by MPVC was faster than that of SPVC un-

TABLE IV  
Specific Surface Areas of the PVC Resins

	M3	S3
Specific surface area ( $\text{m}^2/\text{g}$ )	$1.4773 \pm 0.0146$	$1.2681 \pm 0.0639$



**Figure 6** Scanning electron micrographs of MPVC and SPVC particle sections.

der the conditions of the same temperature and the same recipe. The quantity of plasticizer absorption by MPVC resins was much higher than that of SPVC resins at same temperature. So for dry blending, MPVC was more suitable for preparing the PVC slush powder.

2. The type of PVC resin significantly affected the absorption of plasticizer by resins, whereas the particle size and size distribution were almost independent of it.
3. The morphology of PVC particles explained the difference in the plasticizer absorption behavior. There was a skin covering the SPVC resin,

whereas the primary particles were directly exposed on the surface of the MPVC particles.

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