

# Effects of Inorganic Nano-Particles on Plasticizers Migration of Flexible PVC

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**ABSTRACT:** The influences of nano-particles (nano-sized CaCO<sub>3</sub> and nano-sized SiO<sub>2</sub>) on plasticizers volatility, solvent extraction stability, and exudation stability of flexible PVC were studied. The results showed that nano-particles could reduce migration of plasticizers, thus improved the ability of anti-migration of flexible PVC.

Further more, nano-sized SiO<sub>2</sub> shows excellent property than nano-sized CaCO<sub>3</sub> in resistance migration of plasticizers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2178–2182, 2010

**Key words:** migration; plasticizer; PVC

## INTRODUCTION

Flexible poly (vinyl chloride) (PVC) has been employed for a wide range of application in food packaging, biomedical, print, construction, etc. Flexible PVC contains large amounts of liquid plasticizer(s). These liquid plasticizers usually are low molar mass compounds such as phthalates, phosphates, trimellitates, adipates, citrates, etc., which can improve flexibility and softness of PVC products. However, these low molar mass plasticizers are easily migrated from flexible PVC products into the external environment.<sup>1</sup> Migration is the movement of a plasticizer within and from a PVC compound into or onto a substrate to which it is held in intimate contact. PVC plasticizers can be released from flexible PVC in different ways<sup>2</sup>:

1. Volatilization from the PVC surface to the air.
2. Extraction from PVC to a liquid in contact with it.
3. Migration from PVC to a solid or semi-solid in contact with it.
4. Exudation under pressure.

As a result, it have negative effects on substrates. There may involve the appearance of problems and

the contamination of the media in contact with PVC. Also, the loss of plasticizer causes changes in the long-term properties of the material as well as possible toxic and biological effects when the plasticizer is transferred to humans.<sup>3</sup>

To solve these problems, researchers have tested several approaches. Post treatment approaches have been shown to successfully inhibit plasticizer migration that involving chemical crosslinking or grafting by gamma radiation or ultraviolet radiation, surface coating, and surface treatment (plasma treatment, glow-discharge, etc.). But these approaches result in deterioration of the physicochemical properties of the resulting PVC products.<sup>4–8</sup> Polymer modification is introduced by blending one or more different polymers to obtain flexibility to PVC, including nitrile rubbers, polyesters, and copolymers.<sup>9,10</sup>

Inorganic particles had acted as filler in plastics for a long term. The high surface area of nano-particles endues the particles peculiar performance, therefore, wide range of use in many fields. In this study, inorganic nano-particles of CaCO<sub>3</sub> and SiO<sub>2</sub> were employed to reduce plasticizer migration of flexible PVC. An obvious decrease of plasticizer migration could be obtained when appropriate inorganic nano-particles are added in flexible PVC.

## EXPERIMENT

### Materials

Diisononyl phthalate (DINP) and trioctyl trimellitate (TOTM) were used as plasticizers. PVC samples were prepared by mixing the PVC resin, the

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plasticizer and the stabilizer in the following proportions: 100 phr (per hundred of resin) of PVC, 50 phr of plasticizer, 5 phr of epoxidized soybean oil (ESO) and 2 phr of thermal stabilizer, no more than 20 phr of nano-sized  $\text{CaCO}_3$  (25–35 nm) or  $\text{SiO}_2$  (20–50 nm).

### Sample preparation

Inorganic nano-particles were churned up with ESO in a high-speed mixer for 30 min. The inorganic nano-particles were dispersed into PVC powder in a mill in order to obtain a homogeneous mixture. Then plasticizers and thermal stabilizer were added in proportion. Mixing operation was carried out unceasingly at a temperature of 100°C for 8 mins. The blends (plasticized PVC) were processed into sheets on a twin-roll mill with the rolls set at a temperature of 160°C, whereas the line speed of roll is 13 m/min. Then the sheets were molded to make plates, which were required for further tests. Molder was heated up at a temperature of 165°C for 5 min. Then plates were placed into molder. The operating temperature was 165°C for 3 min with a pressure of 5 MPa, and then room temperature for 10 min with pressure of 10 MPa.

### Plasticizer migration stability

Plasticizer migration stability was characterized by the amount of plasticizer migrated out of samples to the gaseous phase (volatility), liquid phase (extractability), and contacting solid substrates (exudation) under the certain condition and by the migrating time to clearly determine the degree of plasticizer migration. Compression-molded samples were cut into rounds with 20 mm diameter. Thickness of the test specimens is 0.4 mm migration tests were carried out based on the appropriate American standard testing methods (ASTM). Weight of individual specimens of same composition shall be within a tolerance of  $\pm 10\%$ .

### Volatility stability

Volatility tests were based on ASTM D1203-94. Three specimens (same composition) were equally placed in 250 cm<sup>3</sup> of granular activated carbon, which spread evenly on a container. Then the container was placed upright in the oven. The temperature of the oven is 87°C and the duration of the test is 6 days. At the end of every 24 h period, take the container out of the oven, brush the residual carbon on the surface of specimens, recondition in room temperature for 1 h and reweigh the specimens.

Calculate the volatile loss as follows:

$$\text{weight loss (\%)} = [(W_1 - W_2)/W_1] \times 100 \quad (1)$$

where:  $W_1$  = initial weight of test specimen, and  $W_2$  = final weight of test specimen.

### Solvent extraction stability

Solvent extraction tests were based on ASTM D1239-98. The test conditions were restricted at a temperature of  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  relative humidity. The specimens were immersed in 200 mL of castor oil under the test conditions, or 200 mL of 50°C distilled water, and kept in a completely vertical position and without stirring during the tests. After 24 h, the castor oil extracted specimens were rinsed with absolute alcohol and then wiped up, and the distilled water extracted specimens were also wiped up. Afterward, the two types of specimens were dried under the test conditions in desiccators for 24 h and reweighed. Calculate the extraction loss according to eq. (1) mentioned above.

### Exudation stability

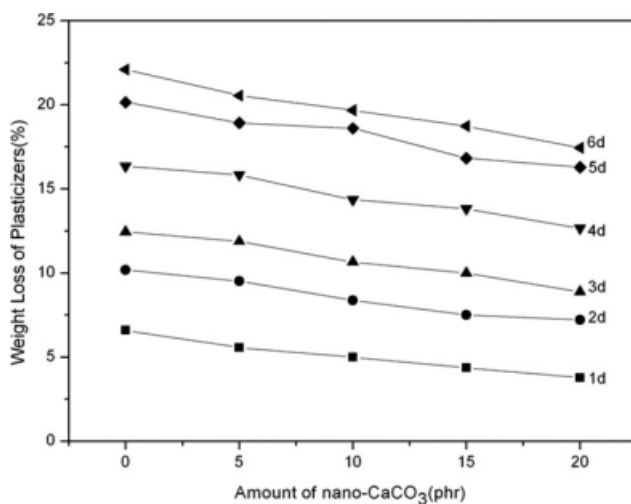
Exudation tests were based on ASTM D2199-82. The specimens were sandwiched between two pieces of high-density polyethylene (HDPE) (same dimension to the specimen and the thickness is 1.5 mm). These "sandwiches" are pressed by 0.125 MPa and placed in an oven at a temperature of  $60 \pm 2^\circ\text{C}$ . Measuring the weight increment of the HDPE sheet after 3 days, the extent of plasticizer exudation can be assessed.

## RESULTS AND DISCUSSION

### Disperse of inorganic nano-particles

A homogeneous dispersion of nano-particles in a polymeric matrix is difficult due to strong agglomeration tendency of nano-particles itself. To break down the nano-particle agglomeration and generate nano-scale dispersion of the particles, ESO was used as compatibilizer to increase compatibility of inorganic nano-particles with PVC resin in this study. ESO also has functions of plasticizer and thermal stabilizer in flexible PVC products.

Because the epoxy group in ESO can be easily bonded with  $-\text{OH}$ , which exists on the surface of nano-sized  $\text{CaCO}_3$  and nano-sized  $\text{SiO}_2$ , so after the inorganic nano-particles were mixed with ESO in a high-speed mixer at 50°C, ESO layers were formed on the surface of the inorganic nano-particles, enwrapping the particles. Then ESO was absorbed by PVC resin quickly whereas the enwrapped inorganic nano-particles were mixed with PVC resin at 100°C, and PVC was swelled and dissolved by ESO, which acts as a plasticizer. After that, a



**Figure 1** Effect of nano-sized CaCO<sub>3</sub> on volatility loss of DINP 1d,2d,3d,4d,5d,6d—time of experiment.

comparatively homogeneous dispersion was achieved between ESO plasticized PVC and inorganic nano-particles.

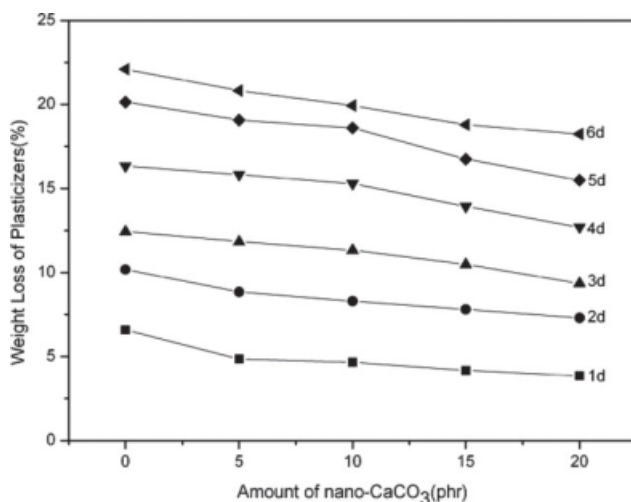
#### Influences of inorganic nano-particles on volatility stability of flexible PVC

Two types of plasticizers DINP and TOTM were employed to study the migration of plasticizers. The volatility loss of plasticizers from flexible PVC containing different amount of nano-sized CaCO<sub>3</sub> or SiO<sub>2</sub> is shown in Figures 1–4, respectively. It can be observed that the volatility loss of plasticizers decreases as the amount of nano-particles increases. Inorganic nano-particles have tremendous specific surface area, and there are quite a number of unsat-

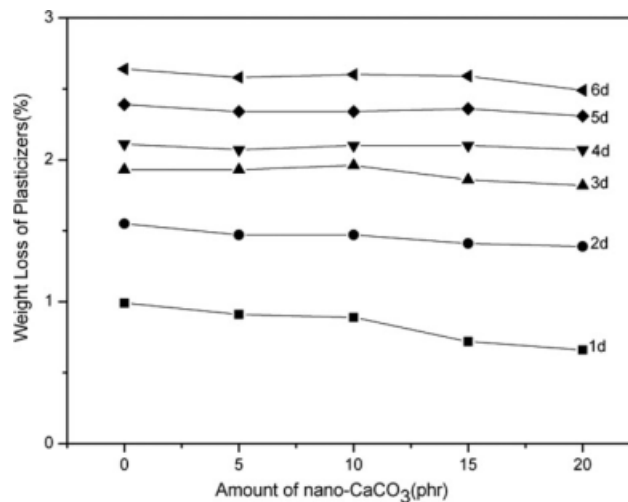
urated surface atoms, which are unstable and high active. Plasticizers are mainly polar molecules, so they are easily combined with the unsaturated bond of the surface atom of nano-particles. The strong binding energy results in hard motion of plasticizer molecules. In addition, inorganic nano-particles are comparatively immovable compared with other components in flexible PVC, so they can restrict the chain movement of plasticizers and simultaneously reduce the contact area of plasticizers with air. As a result, volatility loss of plasticizers decreases.

Comparing Figure 1 with Figure 2, we can see when 5 phr nano-particles were added in flexible PVC with DINP, the volatility loss of plasticizers from flexible PVC containing nano-sized CaCO<sub>3</sub> is larger than the one containing nano-sized SiO<sub>2</sub>. Figures 3 and 4 show the same trend when nano-particles were added in flexible PVC with TOTM, i.e., the efficiency of preventing plasticizer migration of nano-sized SiO<sub>2</sub> is larger than the efficiency of nano-sized CaCO<sub>3</sub>. Nano-sized SiO<sub>2</sub> has a special three-dimensional and porous structure, so there are more deficient-bond atoms on the surface of nano-sized SiO<sub>2</sub>. However, when the amount of nano-particles increases, the dispersion of nano-sized SiO<sub>2</sub> becomes hard owing to its higher surface energy, so no obvious decrement presents when more nano-sized SiO<sub>2</sub> are added.

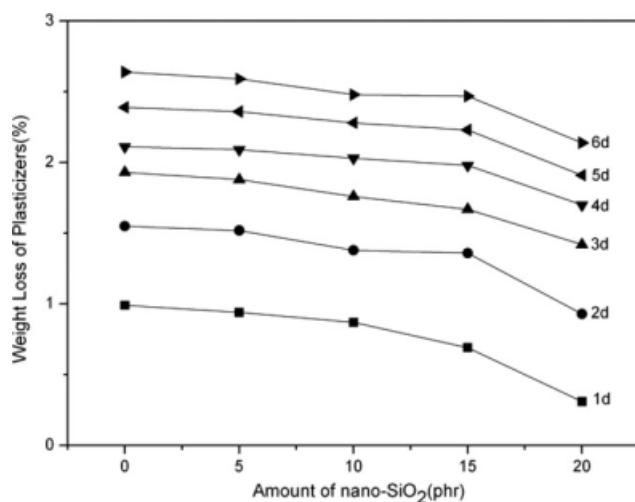
It also observed from the figures that TOTM shows better anti-volatility than DINP, which can be observed according to the volatility loss of the plasticizers. The bulk volume of TOTM is larger than DINP because TOTM has three C<sub>8</sub> chains in its molecule whereas DINP only has two C<sub>9</sub> chains. Branching tends to hinder movement or entangle the plasticizer within the polymer matrix making it more difficult to migrate or be removed by volatilization



**Figure 2** Effect of nano-sized SiO<sub>2</sub> on volatility loss of DINP 1d,2d,3d,4d,5d,6d—time of experiment.



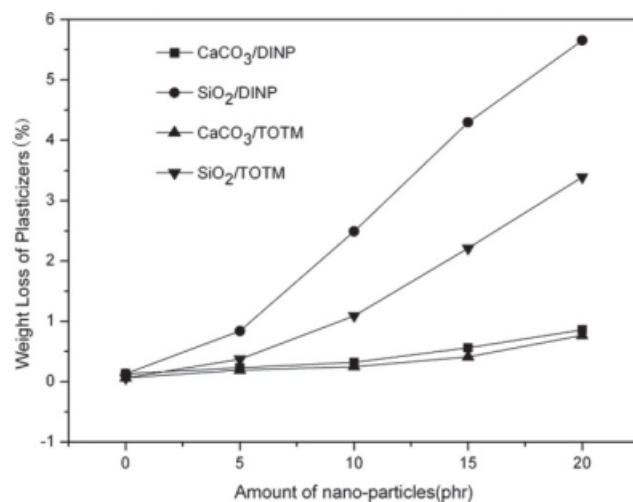
**Figure 3** Effect of nano-sized CaCO<sub>3</sub> on volatility loss of TOTM 1d,2d,3d,4d,5d,6d—time of experiment.



**Figure 4** Effect of nano-sized SiO<sub>2</sub> on volatility loss of TOTM 1d,2d,3d,4d,5d,6d—time of experiment.

or extraction. Simply stated, the longer and bulkier the molecule is, the more difficult for it to be removed. So, DINP is more active than TOTM and easier volatilize to air. When nano-particles are added in compound, volatility loss of DINP decreased sharply because activity of DINP is restrained by nano-particles. The volatility loss of TOTM decreased little owing to less activity of TOTM.

Besides, the influence of time on the plasticizer anti-migration capability of nano-particles can be concluded from the curves in Figures 1–4. More time could increase the volatility loss of plasticizers from PVC samples whether what plasticizer and what nano-particles be used.

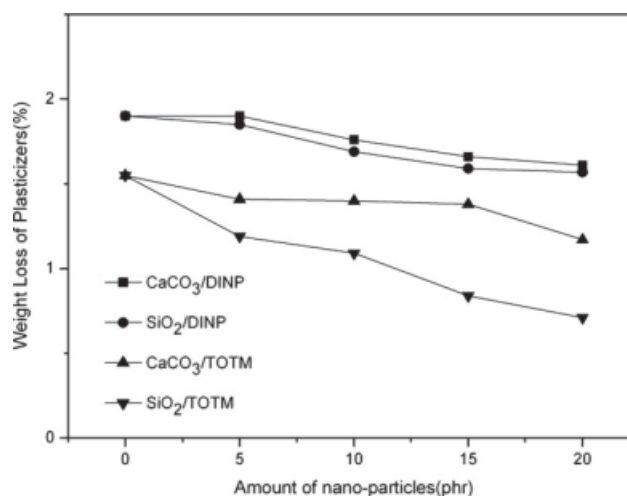


**Figure 5** Effect of nano-particles on extraction loss of plasticizers by distilled water.

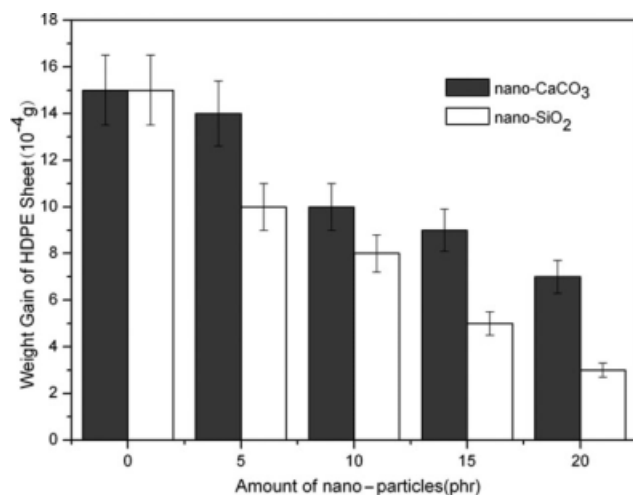
### Influences of inorganic nano-particles on solvent extraction stability of flexible PVC

Plasticizers are easily extracted by surrounding liquids. Figure 5 shows the extraction loss of DINP and TOTM by distilled water from flexible PVC containing different amount of nano-particles. The greater nano-particles were added, the greater extraction loss of plasticizers increases. Water can be absorbed into flexible PVC because nano-sized CaCO<sub>3</sub> is bibulous, which also induced larger contact area with water. Thus, larger amount of plasticizers are extracted by distilled water. Nano-sized SiO<sub>2</sub> is more bibulous than nano-sized CaCO<sub>3</sub> because its three dimensional and porous structure. As a result, plasticizers can be extracted much more easily by distilled water at nano-sized SiO<sub>2</sub> existed.

The effect of nano-particles on extraction loss of plasticizers by castor-oil is shown in Figure 6. The trend of curve is opposite to the effect of nano-particles on extraction loss by distilled water. As the amount of nano-particles increases, the extraction loss of the plasticizer decreases correspondingly. The reason is that castor-oil [C<sub>3</sub>H<sub>5</sub>(C<sub>18</sub>H<sub>33</sub>O<sub>3</sub>)<sub>3</sub>] has bigger molecule volume and less activity compared with water, therefore, it is harder for castor-oil to move through the matrix and be absorbed by nano-particles. Nano-particles occupy the surface area of flexible PVC to hinder the extraction loss of plasticizer. Furthermore, nano-particles have high surface energy and unsaturated bond of atoms, which can bond with polar plasticizers. All the same, nano-sized SiO<sub>2</sub> is still more efficient than nano-sized CaCO<sub>3</sub> for its special three-dimensional and porous structure, and more deficient-bond surface atoms.



**Figure 6** Effect of nano-particles on extraction loss of plasticizers by castor-oil.



**Figure 7** Effect of nano-particles on TOTM exudation to HDPE for 3 days at 60°C/0.125 MPa.

### Influences of inorganic nano-particles on exudation stability of flexible PVC

Plasticizers can be exudates from flexible PVC to contacting solid medium. Figure 7 shows the influences of nano-particles on TOTM exudation from flexible PVC to HDPE for 3 days at 60°C and 0.125 MPa pressure. As can be seen, more nano-particles added in flexible PVC, the less exudation loss of plasticizers obtained. The matter also is nano-particles bonded with polar plasticizer molecules and it's strongly obstructive to molecule movement of plasticizers. Again, nano-SiO<sub>2</sub> is more efficient than nano-CaCO<sub>3</sub> here in preventing exudation of plasticizer for its constructor.

### CONCLUSION

It is concluded from this study that inorganic nano-particles can reduce migration of plasticizers from flexible PVC. This is demonstrated in terms of the reduction of volatility loss, extraction loss, and exu-

dition loss of plasticizers. There is an exception that is nano-particles increase the extraction loss of plasticizers by distilled water because nano-particles are bibulous.

Further more, nano-sized CaCO<sub>3</sub> is much less efficient than nano-sized SiO<sub>2</sub> in hindering migration of plasticizers. Because there are more deficient-bond atoms in the surface of nano-sized SiO<sub>2</sub> than the nano-sized CaCO<sub>3</sub>, which are more active and can easily bond with polar plasticizer molecules. Moreover, nano-sized SiO<sub>2</sub> have three dimensional and porous structure, so it has stronger obstructive function of hindering migration of plasticizers than nano-sized CaCO<sub>3</sub>.

The amount of inorganic nano-particles added in this study is less than 20 phr. Better effect was obtained when more inorganic nano-particles were added. Excess nano-particles are difficult to disperse and may cause the deterioration of the performance of flexible PVC. Thus, a homogeneous dispersion of nano-particles is a key to this approach. ESO has positive effect on increasing the compatibility of nano-particles with PVC resin.

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