

Effect of Silica Particles on Adhesion Strength of Polyvinyl Chloride Coatings on Metal Substrates

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ARTICLE INFO

Article history:

Received: 2016-05-09

Accepted: 2016-10-25

Keywords:

PVC

Plastisol

Silica

Coating

Adhesion

ABSTRACT

The aim of this study was to improve the adhesion performance of plasticized polyvinyl chloride (PVC) coatings on steel substrates by using nanoparticles. For this purpose, the PVC plastisol with different concentration of nano-silica was prepared and applied to bond steel joints. The adhesive strength of the joints was determined by single-lap shear test. Moreover, mechanical properties and microstructure of coating were investigated. The addition of 1wt % nano-silica to plastisol dramatically increased the lap shear strength up to 4-fold, which was an outcome of the compatibilizing effect of silica. Young's modulus and tensile strength of plasticized PVC were slightly increased by adding nanoparticles, as well. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) exhibited higher inclusion size in the coating having higher silica volume which was attributed to the agglomeration of nanoparticles. In the following, the effect of plasticizer composition on the adhesion strength by replacing some parts of dioctyl phthalate (DOP) plasticizer with more polar oil, epoxidized soybean oil (ESO) was examined. Although adding ESO improved the lap shear strength of the neat coating, its effect on the properties of the coatings containing silica was negligible.

1. Introduction

Polyvinyl chloride (PVC) with excellent properties such as good chemical resistance, self-extinguishing properties, resistance to wear and reasonable price is one of the well-known polymers that is widely used in the world. It has a wide range of diverse industrial applications in rigid and flexible forms. One of its particular applications is the coating of textile or metal substrates by plastisol. PVC plastisol is a suspension of

PVC powder in an appropriate plasticizer. For the coating process, plastisol is deposited on a substrate by a coating technique and then upon heating at a particular temperature, PVC particles are swelled with the plasticizer and eventually form a homogenous layer.

The rheological properties of plastisol and mechanical properties of the coatings based on it were studied extensively [1-4]. It was reported that the addition of calcium carbonate and nanoclay to plasticized PVC,

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increased its glass transition temperature and mechanical properties such as Young's modulus, tensile strength, and strain to failure [3-6]. However, a few works have been conducted on the improvement of adhesion of plastisol coatings to different substrates. In coating applications, proper adhesion between the coating and the substrate is vital. The adhesion of PVC to the metallic substrates is inherently poor. Mohseni *et al.* demonstrated that applying amino-silane primer on the metal surface could significantly increase the adhesion of plastisol to this surface [7]. Chaudhury *et al.* stated that the adhesion strength of PVC on the silane primed metal surface was related to the inter-diffusion of the primer and polymer phases [8]. The inter-diffusion thickness was a function of polymer molecular weight, diffusion coefficient and contact time of two surfaces [9, 10]. For direct adhesion of polymer to metal (non-primed metal), the adhesion strength is proportional to the roughness of metal surface up to the level that the surface wettability does not deteriorate [11]. However, the magnitude of adhesion force is related to the fundamental thermodynamic quantities, such as surface free energies of both polymer and metal substrate and the interfacial tension between them [12]. Therefore, the parameters that affect these thermodynamic quantities would have an influence on the adhesion strength. There are some reports about changing the surface energy of coatings by adding pigments and fillers [13, 14].

In spite of the favorable and sometimes unique properties of plastisol-based coatings, little attention has been paid to improving the adhesion of PVC to metal surfaces. The previous studies have been mostly focused on the treatment of metal surface or using different primers. In this work, the effect of

silica nanoparticles addition on the adhesion strength of PVC plastisol coatings to the metal surfaces was investigated. Furthermore, the impact of the combination of plasticizer on the bonding strength of the coatings was also considered.

2. Materials and methods

2.1. Materials and samples preparation

The emulsion type PVC (703 E) with K-Value = 70 was supplied by Saudi SABIC Company. Dioctyl phthalate (DOP) made by LG Chemical and epoxidized soybean oil (ESO) made by Baspar Lia Chemical Company were used as plasticizers. The plastisol was stabilized by barium-cadmium heat stabilizer (LX-267) made by KD Chem Company. Silica nanoparticles with average particle size of 12 nm (Aerosil 200) were provided by Degussa Company.

2.2. Preparation of plastisol

The composition of plastisol was 80 phr DOP, 5 phr ESO and 4 phr the heat stabilizer. Silica was also added in various amounts up to 1 wt % of total plastisol weight. The plastisol was prepared as follows: first, plasticizers and stabilizer were kneaded well with a high-speed mixer for 3 minutes. Then, the silica nanoparticles were slowly added to the mixture and mixed for 10 minutes at 3000 rpm. The silica was then homogeneously dispersed by sonication for 30 minutes. In the following, the PVC powder was slowly added to the mixture under high speed mixing at 2000 rpm, and was mixed for about 15 minutes. The control sample (without silica) was also prepared for comparison. In order to de-bubble the obtained mixture was placed under 0.7 bar vacuum for 4 hours.

2.3. Coating preparation

The steel sheets were cut to 125mm×25mm

and their surfaces were cleaned and treated before bonding. The surface treatment was performed based on ASTM D3933 standard. According to this standard, the metal sheets were placed into a solution of hydrochloric acid (50 wt %) at room temperature for 10 minutes. Then, they were immediately neutralized by washing with deionized water. In the following, they were quickly dried with a dry tissue. Lap shear joints were prepared by bonding two metal sheets by plastisol and curing at 170 °C for 10 minutes. The adhesive thickness was about 60 μ m, and the area of adhesion was 3.1 cm². The overlap length of the sheets was 12mm. All samples were then put at room temperature for at least one day before tests.

2.4. Conducted tests

The single lap shear test was performed according to ASTM D1002 standard at a constant cross-head speed of 1.3 mm/min up

to the final failure of the joint using an electromechanical universal testing machine, GOTECH. Four specimens were tested for each condition.

The mechanical properties including Young's modulus and tensile strength were obtained by a tensile test according to ASTM D638 standard by a cross-head speed of 50 mm/min. The specimen dimensions for the tensile test were 50mm length, 25mm width and 0.9 mm thickness.

The scanning electron microscopy (SEM, Vega II XMU, Tescan) and atomic force microscopy (AFM, ARA-AFM) were applied to investigate the distribution of silica nanoparticles in the coatings.

3. Results and discussion

3.1. Morphology

The SEM images of samples containing different content of nano-silica are illustrated in Fig. 1.

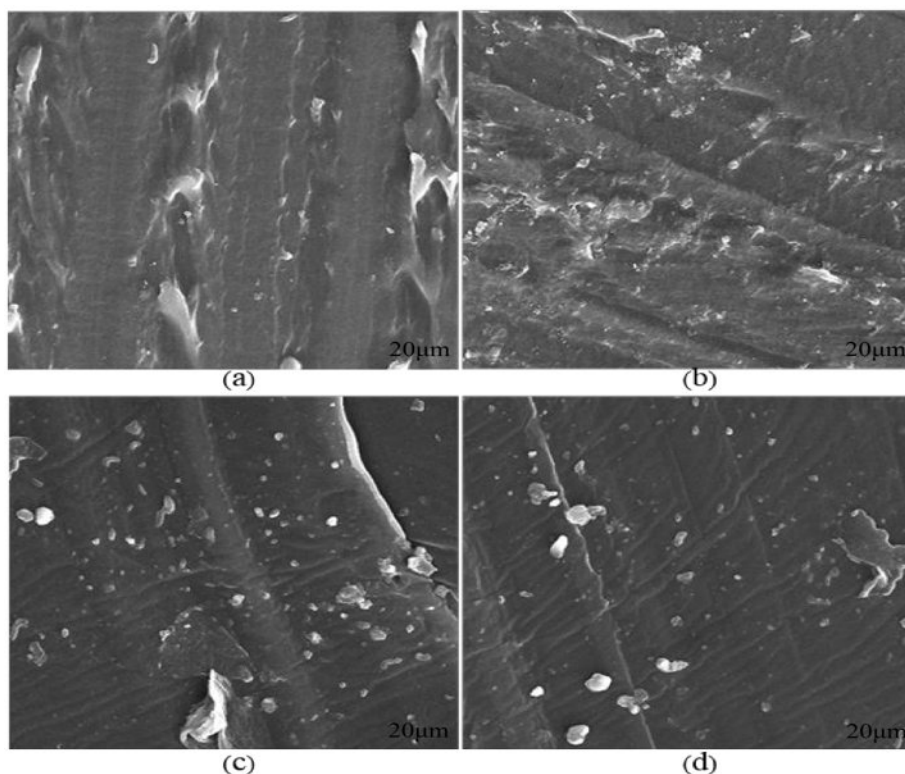


Figure 1. SEM images of the coating containing (a) 0.25 %, (b) 0.5 %, (c) 0.75 % and (d) 1 % silica.

As clearly seen, silica particles were present in the matrix with the size of several tens of nanometers. However, bigger particle size was observed for the samples with higher concentration of silica due to the

agglomeration of silica nanoparticles. Besides SEM images, the AFM micrographs were also taken to consider the morphology of samples (Fig. 2).

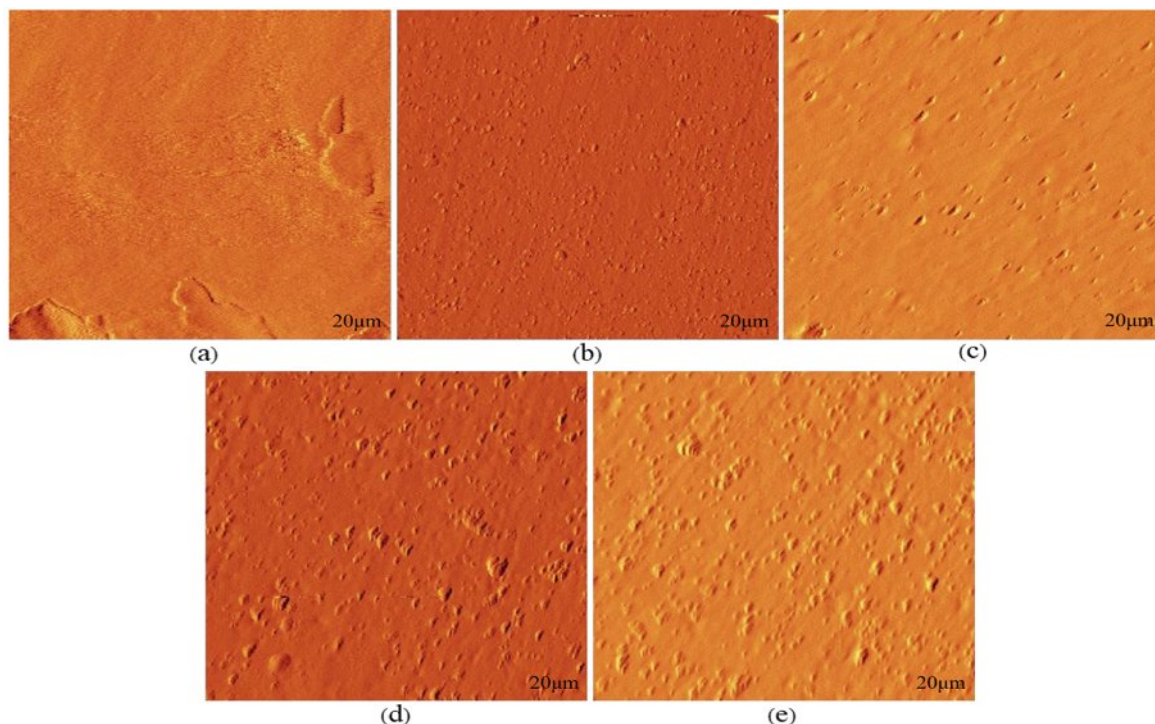


Figure 2. AFM images of (a) neat coating and coating containing (b) 0.25 %, (c) 0.5 %, (d) 0.75 % and (e) 1 % silica.

The AFM images more precisely showed that silica particle size increased as the concentration of silica increased. Accordingly, the range of silica particle size was seen from 30 nm to 800nm. The average particle size was calculated by measuring the diameter of at least 100 particles in different samples and averaging over the data. The mean diameter of particles in coatings including 0.25 %, 0.5 %, 0.75 % and 1 % silica were 147, 306, 377 and 489 nm, respectively, which exhibited more agglomeration of particles in the coatings containing higher silica content.

3.2. Effect of nano-silica on adhesion of the coating to the metallic substrate

The results of stress-displacement in lap shear test of different samples are presented in Fig. 3. The adhesion strength is given by ultimate stress before the break. The adhesion strength was dramatically enhanced from 323 kN/m² for the sample without nano-silica to 1371 kN/m² for the sample containing 1 % nano-silica, indicating more than 4-fold improvement in this property. The displacement to break was increased as nano-silica increased, as well.

The trends of the adhesion strength and displacement to failure versus nano-silica content are displayed in Fig. 4. As clearly seen, both tensile strength and elongation at break were increased with the addition of silica.

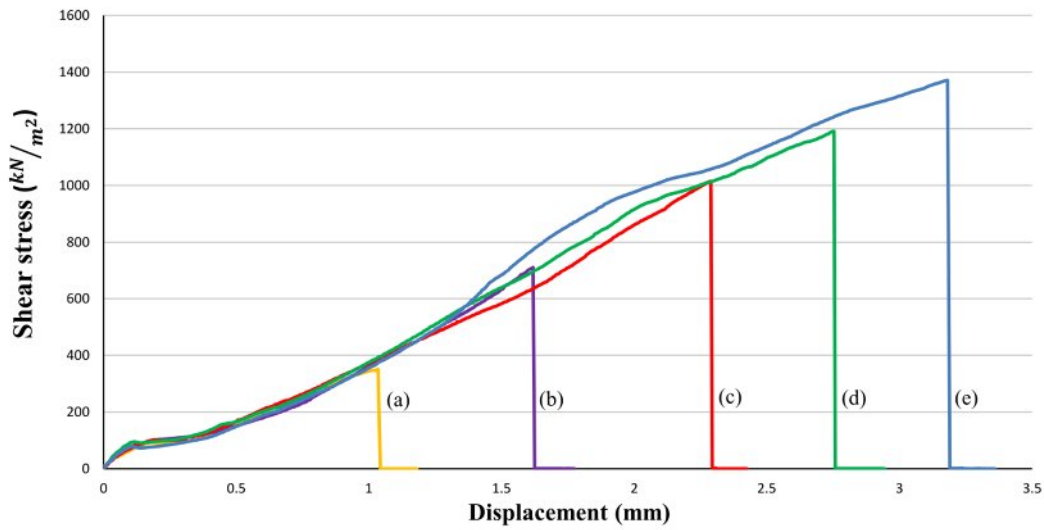


Figure 3. Shear stress vs. displacement in single lap joint test for (a) neat coating and coating containing (b) 0.25 %, (c) 0.5 %, (d) 0.75 % and (e) 1 % silica.

In another research it was reported that adding epoxy resin to plastisol in an optimized condition improved the adhesion strength of the coating up to more than 7-fold

[15]. This significant improvement was a result of chemical bonding between the epoxy resin and the metallic surface.

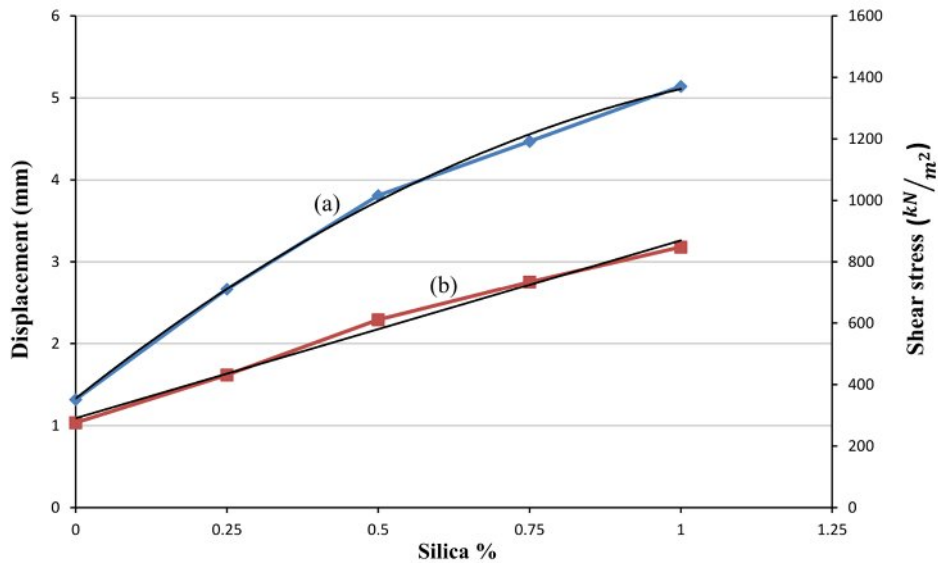


Figure 4. (a) Adhesion strength and (b) displacement as a function of silica content.

However, in our system, silica is a neutral particle and cannot form covalent bonds with the metallic surface. It seems that adding nano-silica led to the polarity of the coating being enhanced. The -OH bonds of silica surface create strong interaction with the

polar metal surface. This caused the compatibility of the polymeric coating and the metallic substrate to advance. There also exists some research that stated adding nano-silica to the PVC coating caused an increase in its surface roughness [14]. Higher surface

roughness could lead to higher mechanical interlocking between coating and substrate, and result in higher adhesion strength. Accordingly, improvement of compatibility between the coatings and the substrate, and the enhancement of surface roughness would be responsible for the significant increase in adhesion strength of the coating including

nano-silica.

3.3. Investigating the tensile properties

The mechanical properties of plastisol coatings containing various amounts of silica were studied by tensile test, and the results are shown in Fig. 5.

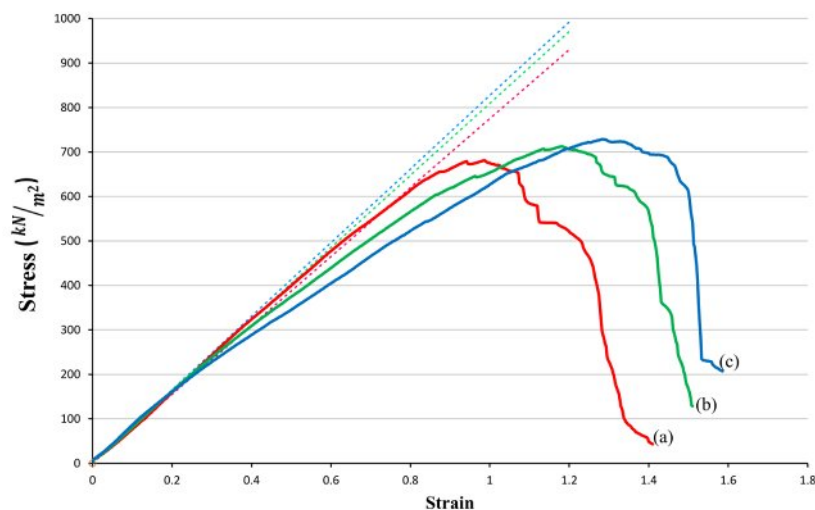


Figure 5. Tensile stress-strain curves of the samples containing (a) 0 %, (b) 0.5 % and (c) 1 % silica.

The stress-strain diagram for the samples containing 0, 0.5 and 1 % silica in the region of low tension (stress less than 150 kN/m²) were very close together. However, Young's moduli of these samples were slightly different. By adding 1 % nano-silica to the coating, tensile modulus and tensile strength were increased by about 7 % compared to the neat specimen (specimen excluding silica). The results of tensile modulus and strength are reported in Table 1.

Table 1.

Tensile properties of the samples.		
Silica content (wt %)	Young's modulus (MPa)	Tensile strength (kPa)
0	7.75	734
0.5	8.09	767
1	8.27	784

Considering these results along with AFM images indicated that the agglomerated nano-silica particles with the sizes below 1 micron (which existed in the samples) did not make a destructive effect on the tensile properties. In another study, Chen and co-workers described that the addition of calcium carbonate nanoparticles to the PVC matrix up to 10 phr increased the tensile strength and modulus.[16] The slight change in tensile properties of coatings including nano-silica helped us to understand that the dramatic enhancement in the adhesion strength of these coatings was not related to the reinforcement of the coating itself (or improving cohesion strength). But, this improvement was a result of promoting (physical) interaction between these coatings and metal surfaces, indicating that silica acted as an efficient compatibilizer in this system.

3.4. Investigation of the oil effect

In the following, the impact of oil composition on the adhesion strength of the neat coating and composite coating

containing 0.75 % silica were investigated by replacing ESO instead of some parts of DOP. The results of lap shear test for neat coating are shown in Fig. 6.

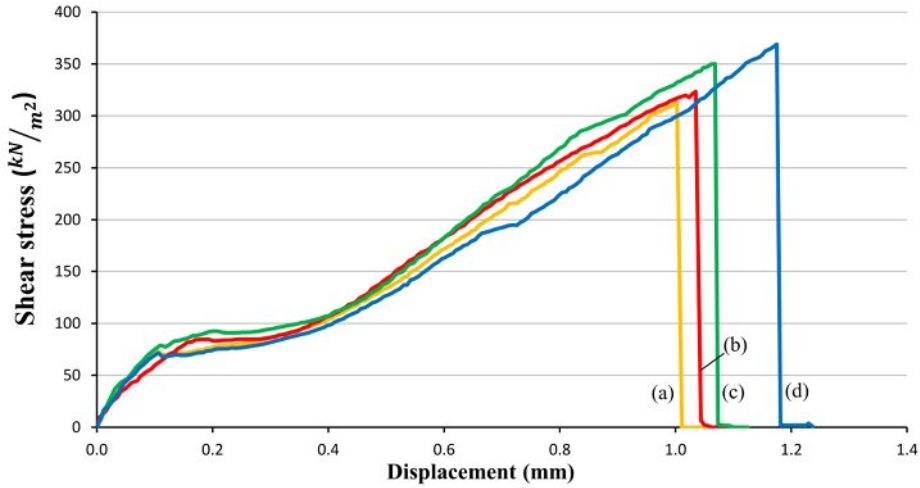


Figure 6. Shear stress vs. displacement in single lap joint test for the neat coating containing (a) 0 phr, (b) 5 phr, (c) 10 phr and (d) 42.5 phr ESO.

As seen, the adhesive strength of the coatings was increased incessantly by increasing ESO content. The replacement of half the oil content with ESO caused about 20 % increment in the adhesion strength and failure strain which would be related to the higher polarity of ESO compared to DOP. In

the composite coating, including 0.75 % of silica, the adhesion strength and failure strain were increased by approximately 6 % and 19 %, respectively (Fig. 7). These results exhibited that in the presence of silica, the impact of oil composition on the adhesion properties was diminished.

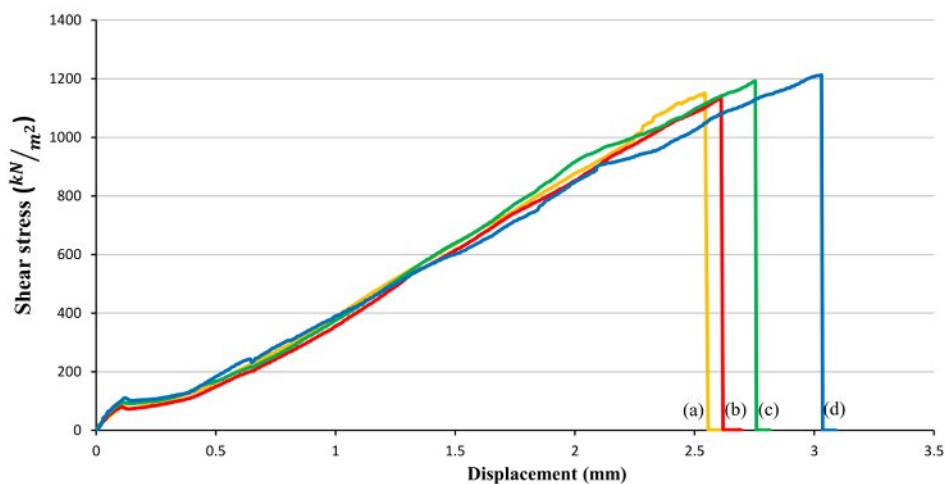


Figure 7. Shear stress vs. displacement in single lap joint test for the coating includes 0.75 % silica and (a) 0 phr, (b) 5 phr, (c) 10 phr and (d) 42.5 phr ESO.

4. Conclusions

The effect of nano-silica on the adhesion strength of plastisol coatings to the metal substrate was investigated. The SEM and AFM images of samples simultaneously showed a range of particle size between 30 to 800 nm. The coating with higher silica content possessed larger particle size, which was related to the more agglomeration of nanoparticles. By adding 1 % nano-silica to the plastisol, the adhesion strength of the coating on the metal surface was dramatically increased up to 4-fold as a result of compatibilizing effect of the silica. In addition, the tensile modulus and tensile strength of samples were slightly increased. Moreover, the effect of oil composition on the adhesion strength of the coatings including and excluding silica was also investigated. The adhesion strength and failure strain of both coatings were increased by replacing ESO instead of some part of DOP. However, the impact of oil composition on the adhesion strength of the coating including silica was diminished.

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