# Poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride)/ Silica Nanocomposites Derived from *In Situ* Suspension Polymerization

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**ABSTRACT:** Poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride) (PVVM)/silica nanocomposites were prepared by the suspension radical copolymerization of the monomers in the presence of fumed silica premodified with γ-methylacryloxypropl trimethoxy silane. Morphological observation showed that the silica particles of nanometer scale were well dispersed in the copolymer matrix of the nanocomposites films, whereas silica particles tended to agglomerate in the composites films prepared by the solution blending of PVVM with silica. The experimental results show that the thermal stability, glass-transition temperature, tensile strength, and Young's modulus were significantly enhanced by the incorporation of silica nanoparticles. The enhancement of properties was related to the better dispersion of silica particles in polymer matrix and the interaction between the polymer chains and the surfaces of the silica particles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3764–3771, 2012

**Key words:** mechanical properties; nanocomposites; thermal properties

## INTRODUCTION

Poly(vinyl chloride-*co*-vinyl acetate) is commonly used in coatings, such as protective paints for metals, because of its high corrosion resistance, good flame retardance, optimum solubility, and low cost. Recently, poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride) (PVVM) has attracted considerable attention because of its better adhesive ability.[1] Solution polymerization is the conventional method of producing PVVM. A novel approach by aqueous suspension polymerization has also been developed to prepare PVVM.[2] However, introducing vinyl acetate elements into poly(vinyl chloride) (PVC) chains decreases the heat resistance and mechanical properties because of the flexibility of ester groups and the reduction of chlorine content. Therefore, it is significant in terms of application to improve the heat resistance and to strengthen the mechanical properties of PVVM.

Recently, to improve the distinct properties of polymers, a large number of studies have been directed toward the functionalization of polymers with nanofillers or by the creation of zero- to two-dimensional structures. For example, many nanoscale inorganic particles have been introduced into the polyamide 6 matrix to improve its properties, among which materials based on spherical particles, such as silica and titanium, and materials based on layered silicates, such as montmorillonite and mica, have been studied extensively.[3] Acrylic-based polymer nanocomposites and polyolefin–clay nanocomposites were reviewed by Wang et al.[4] and Pepmicek et al.,[5] respectively. Novel mechanical, thermal, optical, electrical, and magnetic properties were conveniently brought into those polymer-based nanocomposites. With regard to nanocomposites of PVC, a few studies have been reported to date. It was found that the addition of nanoscale inorganic fillers, for example, $SiO_2$,[6–10] clay,[11,12] montmorillonite,[13–15] $CaCO_3$,[16] and kaolin,[17] into the PVC matrix improved the thermal, rheological, and mechanical properties of the composites. The effects of the surface modification of the inorganic filler on the morphology and properties of PVC composite have been investigated extensively.[6,9–11,17] Blending[6,9,11] and *in situ* polymerization[12,14–16] are two of the major methods used to incorporate inorganic particles into PVC or copolymers of vinyl chloride monomer (VC). Usually, the products made by the latter method

show a well-dispersed morphology. The improvement of the thermal and mechanical properties of a few copolymers of VC due to the incorporation of nanoscale inorganic fillers has also been reported.[18–20] For example, Allie[20] evaluated the corrosion protection, mechanical, and thermal properties of nanosilicate-filled poly(vinyl chloride-co-vinyl acetate) coatings and showed that the nanocoatings improved the thermal barrier properties compared to the neat copolymer.

Until now, to the best of our knowledge, there has been no work reported on the nanocomposites of PVVM/silica. The purpose of this study was to prepare PVVM/silica nanocomposites by the *in situ* suspension polymerization of the monomers in the presence of silica and to further study the influence of silica on the properties of the nanocomposites. Furthermore, the results were compared with the properties of a composite prepared by simple blending.

## EXPERIMENTAL

### Materials

VC, with 99.99 wt % purity, was provided by Shanghai Chlor-Alkali Chemical Co., Ltd. (Shanghai, China). Vinyl acetate and maleic anhydride were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Vinyl acetate was purified by distillation. The γ-methylacryloxypropyl trimethoxy silane (MPS) was supplied by Nanjin Shuguang Chemical Plant (Jiangsu, China) and was used without further purification. The fumed nano-$SiO_2$ particles, with a specific surface area of 200 $m^2$/g, were purchased from Degussa Co., Ltd. (Dusseldorf, Germany).

The fumed nano-$SiO_2$ particles were modified by MPS according to the method discussed in refs. 6 and 21. The γ-methylacryloxypropyl trimethoxy silane modified silica nanoparticles (MTS) were characterized by thermogravimetric analysis (TGA). The weight loss at 800°C was approximately 12.6%; this resulted from the thermal decomposition of the grafted MPS molecules on the silica surface.

### Preparation of PVVM

The PVVM sample was prepared according to a procedure described previously.[2] In brief, VC, vinyl acetate, maleic anhydride, desalting water, a dispersing agent, and an initiator were mixed and stirred in a 10-L autoclave at 60°C for 6 h to a conversion of 85%. Unreacted monomers were removed by degassing, filtration, washing, and drying. The obtained resin had an average particle size of 120 μm and a polymerization degree of 700. The molar ratio of VC to vinyl acetate to maleic anhydride in the resin was 85 : 13 : 2, where the content of maleic anhydride was calculated from the acid value.

### Preparation of the PVVM/silica composites by *in situ* polymerization

The PVVM/silica composites were prepared by polymerization of the previous monomers in the presence of MTS. The range of $SiO_2$ loading levels was from 0 to 5.0 wt %. The procedure and formulation were the same as for the preparation of PVVM, except that an appropriate amount of MTS was added. These products are abbreviated as SPC-I in this article.

### Preparation of the composite films

Films of PVVM/silica composites from *in situ* polymerization were prepared as follows: 20 g of the SPC-I sample was dispersed into a mixed solvent of 40 g of toluene and 40 g of butanone and stirred for 12 h to form a solution. By casting the solution in a polytetrafluoroethylene mold, we obtained films of 0.8–0.9 mm thickness.

Films of the PVVM/silica composites from blending were prepared similarly. The PVVM sample (20 g) and certain amount of MTS were dispersed into a mixed solvent of 40 g of toluene and 40 g of butanone and stirred for 12 h to form a solution. The solution was also cast in a polytetrafluoroethylene mold. After the solvent evaporated, films of the blended composite (abbreviated SPC-B) with thicknesses of 0.8–0.9 mm were formed.

### Measurements

The Fourier transform infrared (FTIR) spectra of samples were recorded on a PerkinElmer Spectrum-1 FTIR spectrometer (PE Corp., California, USA) with KBr pellets in the wave-number range 4000–400 $cm^{-1}$. TGA was performed with a PerkinElmer TGA-7 (PE Corp., California, USA) under a stream of nitrogen at a scan speed of 10°C/min. The glass-transition temperature ($T_g$) was measured on a PerkinElmer DSC-7 (PE Corp., California, USA) thermal analysis system under a nitrogen atmosphere at a heating rate of 10°C/min. The morphology of the freezing microtome sections of the composite films was observed with a transmission electron microscope (JEM-2010, JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 200 kV. The average particle size of the resin was measured with a laser light-scattering granularity instrument (Mastersizer-2000, Malvern Instruments Ltd., UK) in the range from 0.02 to 2000 μm.

Viscosity measurements of the solutions (20 wt %) were carried out at room temperature with a cylinder rotating viscometer (DNJ-79, Tongji University

Electromechanical Plant, Shanghai, China). The shear rate was kept at 350 s$^{-1}$.

Heat aging was performed in an aging oven at 160°C for 10 min. The whiteness was measured by a whiteness meter (WSB-L, Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) equipped with a 457-nm blue ray filter, which was calibrated by a standard white plate. So the collected data was blue ray whiteness. The test range of whiteness data was 0–100%.

The tensile properties of the films were determined with an Instron-4466 tester (Instron Corp., MA, USA) at a crosshead rate of 100 mm/min. Solutions of the composite samples were coated on an aluminum plate, and the properties of impact and adhesive force were measured, respectively.

The impact strength of paint was measured by a drop hammer impact machine (QJ, Tianjin Zhongya Material Testing Plant, Tianjin, China). The 1000-g drop hammer with a steel ball was dropped from various heights in the range 0–50 cm to strike the paint. The impact strength was evaluated by the integrity degree of the paint. Here, the impact value was the maximum height at which the hammer was dropped in which the paint remained intact. The higher the value that was gained, the better the impact strength was.

The adhesion force was measured by wear-resisting needle-tip circling (QFZ-II, Tianjin Zhongya Material Testing Plant, Tianjin, China) on the paint film surface. The scratch trace was divided into seven parts. Every part was ordinally examined to judge the integrity of the trace. We considered that the part was good if 70% of the circle did not crack. Every part corresponded separately to one grade. Grade 7 was best, and grade 1 was worst.

## RESULTS AND DISCUSSION

### Characterization of the PVVM/SiO$_2$ nanocomposites

Figure 1 shows FTIR spectra of PVVM [Fig. 1(a)], SPC-I with 3 wt % silica [Fig. 1(b)], MTS [Fig. 1(c)], and the insoluble residue of SPC-I with 3 wt % silica [Fig. 1(d)], which was obtained by the removal of PVVM from the composite through extraction with acetone for 24 h. From the spectrum [Fig. 1(b)], it could be seen that there was a pronounced band at 1102 cm$^{-1}$, corresponding to the vibration absorption of Si—O—Si groups. The same absorption band could not be found in the PVVM spectrum [Fig. 1(a)]. The results indicate that the silica was incorporated into the polymer after *in situ* polymerization.[7] Through a comparison of the spectrum (c) with spectrum (d), it is clear that their characteristic bands were completely the same. These results imply that the insolu-
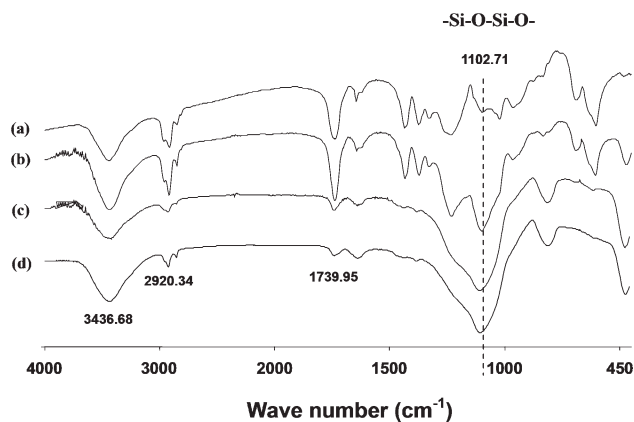


**Figure 1** FTIR spectra of (a) PVVM, (b) SPC-I (3 wt % SiO$_2$), (c) MTS, and (d) insoluble residue of SPC-I (3 wt % SiO$_2$).

ble residue of the composite was MTS and confirm that the SPC-I sample contained silica. Spectrum (d) also revealed that almost no grafting occurred during the *in situ* polymerization.

The distribution of silica particles in the composites was investigated with transmission electron microscopy. The results are shown in Figure 2. As can be seen in Figure 2(a,b) for SPC-I films, the silica particles with a size on the nanometer scale were well dispersed in the PVVM matrix. Shown in Figure 2(c,d) are the composite films prepared by the simple blending of PVVM and MTS, coded as SPC-B films. The agglomeration of silica particles was found.

When SPC-I was prepared, silica was added to the monomers and stirred. Because of the low viscosity of the monomer mixture, the silica particles were well dispersed in the mixture. However, for SPC-B, silica was added to the viscous solution of PVVM. The high viscosity of the solution prevented the silica particles from being uniformly dispersed. This is the reason why more agglomerations of the inorganic particles were observed in the SPC-B films.

### Solution viscosity

PVVM is usually used as an adhesive substance in paint. So the solution viscosity of PVVM/silica composites may affect the performance of the product directly. Toluene and methyl ethyl ketone are often used as components of mixture solvents for PVVM. The effect of the silica content on the solution viscosity of the composites is shown in Figure 3. It can be seen that the incorporation of the silica particles increased the solution viscosity of SPC-I and SPC-B. The increase in the viscosity with the addition of silica particles was consistent with classical rheology stemming from the pioneering work that if a rigid filler material is added to a suspension, the shear viscosity will be increased.[22]
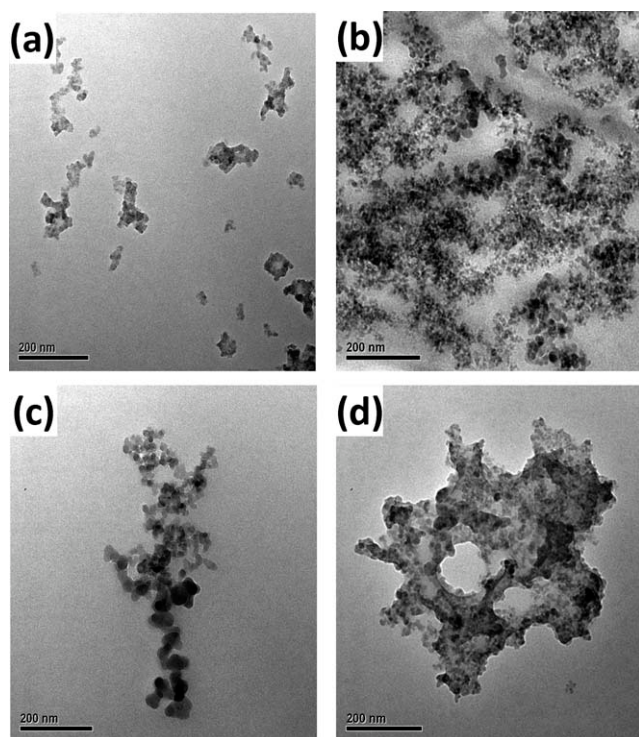
**Figure 2** Transmission electron micrographs of the composite films: (a) SPC-I with 1 wt % $SiO_2$, (b) SPC-I with 5 wt % $SiO_2$, (c) SPC-B with 1 wt % $SiO_2$, and (d) SPC-B with 5 wt % $SiO_2$.

It can also be seen from Figure 3 that the solution viscosity of SPC-I was higher than that of SPC-B at the same silica content. This could be attributed to the uniform dispersion of silica particles and the greater number of interfaces between the filler particles and matrix in SPC-I. The interaction on the interfaces impeded the movement of molecules in solution. At higher filler contents, a slight decrease in the viscosity of both SPC-I and SPC-B were observed. This could be ascribed to the agglomeration of filler particles in the samples with higher filler contents, as shown in Figure 2. A greater nano-$SiO_2$ loading resulted in a higher particle volume density and higher solution viscosity. When the particle volume density increased to a certain extent, the probability of collision and contact between nanoparticles became higher. Because of the high surface energy, the nanoparticles were easy to agglomerate and formed larger particles in the polymer solution. The agglomerate reduced the specific surface area of general particle internal friction between particles and polymer solution; this resulted in a decreased solution viscosity. So when the nano-$SiO_2$ loading was increased to a high degree, the solution viscosity decreased instead.

## Thermal properties

The stability and degradation behavior of PVVM were close to those of PVC because its main mono-
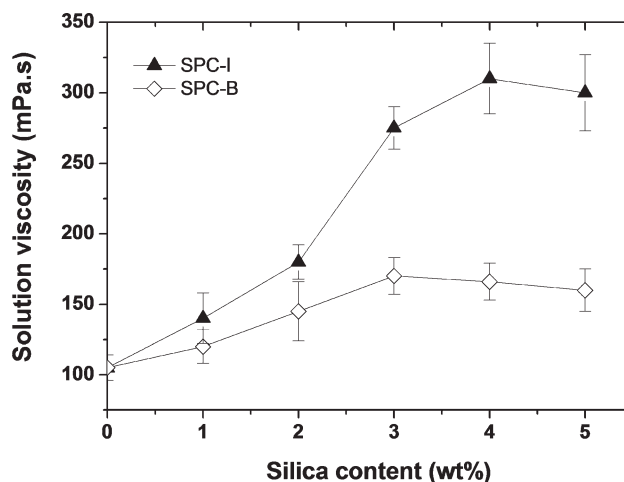


**Figure 3** Plots of the solution viscosity of the composites as a function of silica content at room temperature (20 wt % concentration in a solvent of 50/50 toluene/methyl ethyl ketone).

mer was VC. Dehydrochlorination occurred at high temperature. HCl molecules were easily broken away from the PVVM chain, and then, the unstable polyene configurations were formed. The polyene structure accelerated polymer degradation and damaged the mechanical properties of the polymer. The resin became yellow and/or brown because of the unsteady polyene component absorbing light. The amount of polyene configurations had a significant effect on the color of the resin. So there was a definite relationship between the whiteness value and the heat-resistant ability. It was useful to introduce a whiteness value to show the thermal stability of PVC, PVVM, and their composites containing chloride. The higher the whiteness value that was gained, the better the thermal properties were.

The measurement results of the PVVM/silica nanocomposites and blends are shown in Figure 4. It
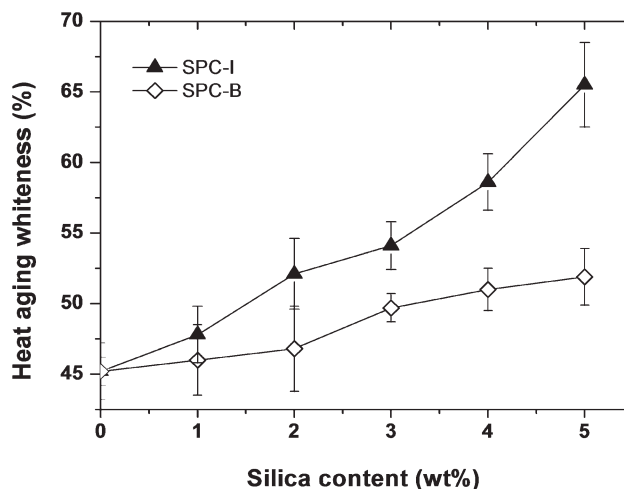


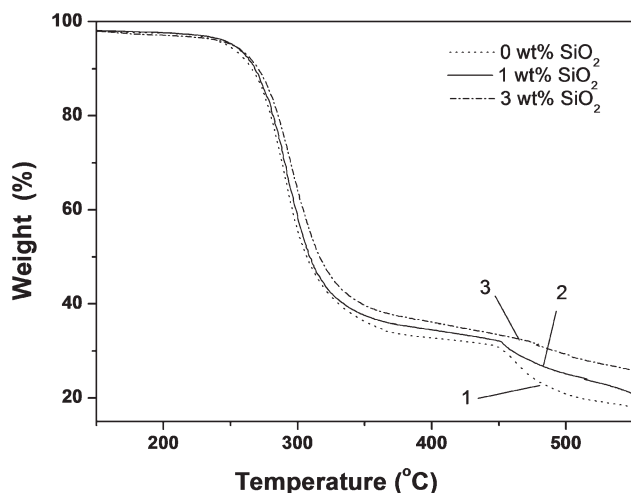**Figure 4** Influence of the silica content on the whiteness of SPC-I and SPC-B after heat-aging of 10 min at 160°C.

**Figure 5** Thermogravimetric curves for the PVVM/silica composites with $SiO_2$ contents of (1) 0, (2) 1.0, and (3) 3.0 wt %.

can be seen that the heat-aging whiteness escalated with increasing silica content. The results indicated that the thermal stability of PVVM was improved with the incorporation of silica particles. As can be also found in Figure 4, the whiteness values of the *in situ* composite were higher than those of the blending composite. Compared with the blending composite, nano-$SiO_2$ distributed more uniformly in the bulk polymer by *in situ* polymerization. The volume density of the particle was higher, and the particle size was smaller. Nano-$SiO_2$ was entwisted with the molecule chain and made the speed of dehydrochlorination slower during heating. The component of the unsteady polyene structure decreased. So the nanocomposites showed better whiteness values than the blends.

The thermal stability and degradation behavior of PVVM and its composites with various $SiO_2$ loadings in a nitrogen environment were also investigated by TGA. The results are shown in Figure 5. Similar to PVC, PVVM and its nanosilica composites exhibited two-stage degradation. The first stage was attributed to dehydrochlorination followed by the formation of the conjugated polyene sequences, whereas the second stage corresponded to the thermal cracking of the carbonaceous conjugated polyene sequences.[15,18,23] From the TGA curves, the temperature at 20% weight loss ($T_{20\%}$) and the temperature at 50% weight loss ($T_{50\%}$) were collected and are summarized in Table I. $T_{20\%}$ and $T_{50\%}$ corresponded to the course of dehydrochlorination and backbone degradation, respectively. It can be seen in Table I that both $T_{20\%}$ and $T_{50\%}$ of the composites shifted toward higher temperatures with increasing $SiO_2$ content. The results indicate that the dehydrochlorination and backbone degradation of PVVM were delayed with the addition of silica particles.

**TABLE I**
**TGA Results of the PVVM/Silica Composites**

| Sample | $T_{20\%}$ (°C) | $T_{50\%}$ (°C) | Residual weight at 500°C (%) |
|---|---|---|---|
| PVVM | 279 | 306 | 20.9 |
| SPC-I (1.0 wt % $SiO_2$) | 281 | 309 | 25.1 |
| SPC-I (3.0 wt % $SiO_2$) | 285 | 316 | 29.3 |

The enhanced thermal stability detected by TGA was consistent with the test results of whiteness in heat aging shown in Figure 4. The residual weights of PVVM and the composites at 500°C are also listed in Table I. The difference in residual weight percentage between the composite and PVVM was obviously greater than the weight percentage of silica content, as shown in Table I. This implied the existence of interaction between the silica nanoparticles and PVVM matrix, which delayed the dehydrochlorination and backbone degradation of polymer molecules and resulted in enhanced thermal stability. Such effects have been reported for a series of polymer nanocomposites.[18] They enable the matrix polymer to be more stable under heating.[15,16] In the system of PVVM/silica, the interaction between the silica particles and PVVM matrix probably originated from the special interaction between VC units in PVVM and the carbonyl groups of MPS grafted on the silica surface through the reaction with silanol groups of silica.

Figure 6 shows the differential scanning calorimetry (DSC) thermograms of PVVM and the PVVM/$SiO_2$ nanocomposites. The $T_g$ values of SPC-I with 1.0 wt % $SiO_2$ and SPC-I with 3.0 wt % $SiO_2$ were 68.1 and 70.3°C, respectively, which were higher than that of neat PVVM (58.9°C). The results of DSC measurement indicate that the heat resistance of
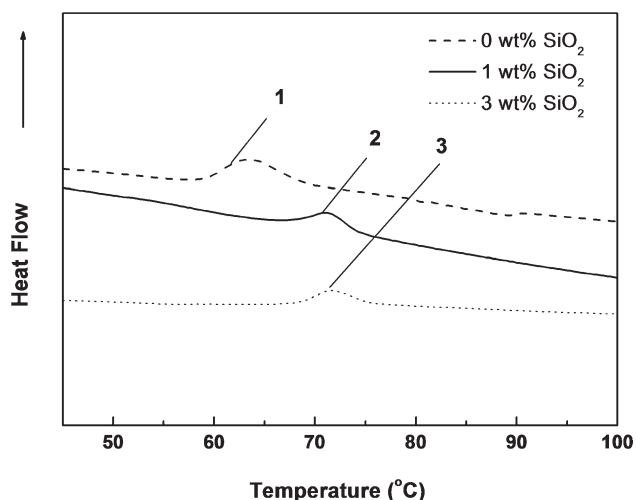


**Figure 6** DSC curves of the PVVM/silica composites with $SiO_2$ contents of (1) 0, (2) 1.0, and (3) 3.0 wt %.
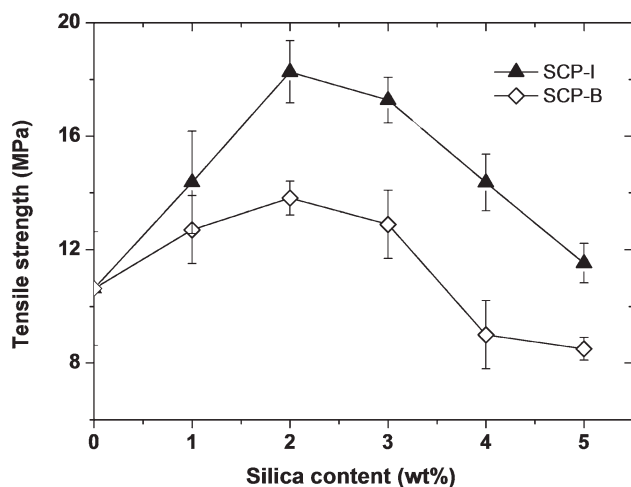
**Figure 7** Effect of the silica content on the tensile strength of the composite films.

PVVM was improved by the incorporation of silica particles. The rigid silica particles themselves[19] and the interaction between the filler particles and matrix[16,24] restricted the molecular mobility of the polymeric segments near the silica surface and resulted in higher $T_g$ values.

## Mechanical properties

The effects of the silica weight fraction on the tensile strength and Young's modulus of the composites are shown in Figures 7 and 8, respectively. For SPC-I and SPC-B, with increasing silica weight fraction, the tensile strength and Young's modulus first increased to maximum values at 2 wt % and then decreased gradually. The tensile strength and Young's modulus of SPC-I were greater than those of the SPC-B composites at the same silica weight fraction. The optimum values of tensile strength and Young's modulus of SPC-I were twice as high as
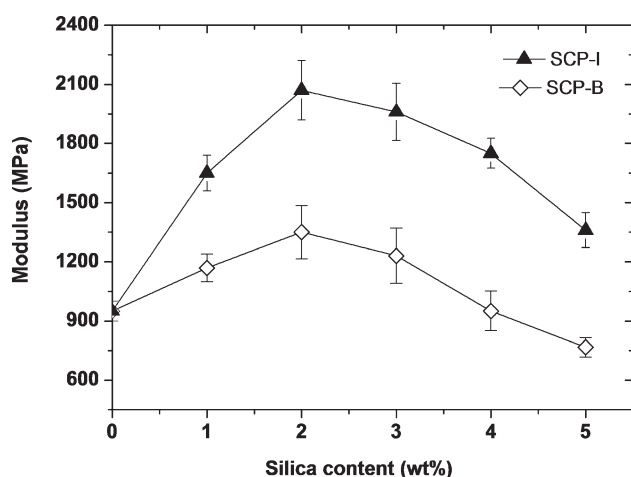
those of PVVM. The results show that the mechanical properties of PVVM were improved significantly with the incorporation of silica particles. The enhancement in the tensile properties could be attributed to the higher modulus of the nanofiller and the interaction between the polymer molecules and the surfaces of the filler particles, as reported previously.[18,19] It is believed that the interaction improved adhesion between the polymer matrix and the filler, which was crucial to stress transfer between these two phases.

As Figure 2 shows, more agglomeration of silica particles occurred in the SPC-B film. The aggregation of inorganic particles in the matrix reduced the effective interfacial interaction, and thus, physical defects were formed in the composites. This is believed to be the reason for the lower tensile properties of the SPC-B film.[18] Similarly, the deterioration of the Young's modulus as more silica was incorporated was attributed to the occurrence of more agglomeration of silica particles, as shown in Figure 2.

It has been known that inorganic particles can improve the toughness of polymer nanocomposites, but the effectiveness of the particles depends on both the concentration and suitable interfacial interaction of the filler. The toughening mechanism has been extensively discussed.[24–26] Generally, it is attributed to the shear yielding caused by the stress concentration around the filler particles.

Figure 9 shows the impact strength as affected by the weight fraction of silica in the SPC-I and SPC-B films. Obviously, the impact strength of both SPC-I and SPC-B increased with increasing silica content. In addition, the impact strength of the SPC-I film was greater than that of SPC-B film at the same silica content. As the weight fraction of silica was increased to 4.0 wt %, the impact strength of the
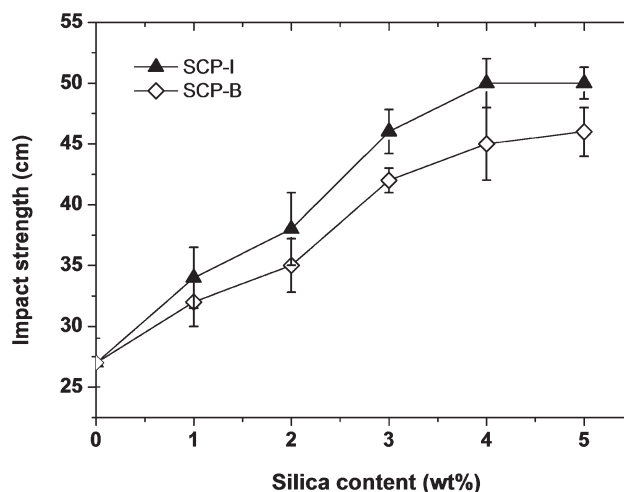


**Figure 8** Effect of the silica content on the modulus of the composite films.



**Figure 9** Effect of the silica content on the impact strength of the PVVM/silica films.
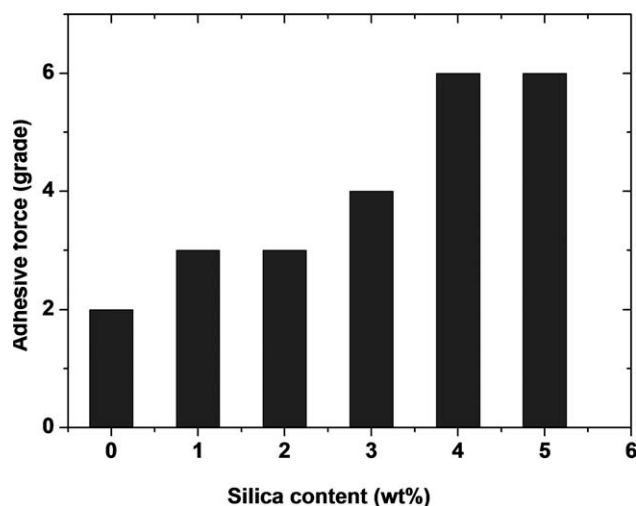
**Figure 10** Effect of the silica content on the adhesive force of the PVVM/silica films.

film reached a high value. Further increases of the silica loading had little influence on the impact strength. The difference between the SPC-I and SPC-B films in impact strength was related to the dispersion of silica particles in the PVVM matrix. The agglomeration of silica particles weakened the toughening effect for introducing defects and reducing interaction on interfaces.

### Adhesion behaviors

The adhesion ability of PVVM is important for its application in paint. Figure 10 shows that the adhesive force between the SPC-I film and an aluminum sheet increased with an increase in the weight fraction of silica particles and reached a maximum at a silica loading of 4 wt %. The optimum values of the adhesion force of SPC-I were three times that of PVVM. The results show that the adhesion ability of PVVM was considerably enhanced by the incorporation of the silica particles. The enhanced adhesion properties could be attributed to an increase in the cohesiveness of the materials caused by the interactions between the polymer chains and silica particles. The enhanced adhesion force prevented the paint from crinkling and brushing off; thus, the paint acted as anticorrosive material to protect the metal. $SiO_2$ particles in the bulk polymer fortified the nanoparticle surface effect. The cohesive energy between the $SiO_2$ particles and copolymer chains was enhanced, and the interface area between the paint and metal surface was also increased. There were chemical and physical effects coexisting in these two phases. These factors resulted in an increased adhesion force with increasing $SiO_2$ loading.

## CONCLUSIONS

In this work, PVVM/silica nanocomposites were prepared by the suspension polymerization of monomers in the presence of fumed silica. The morphology and properties of the PVVM/silica composites gained from *in situ* polymerization were studied to give useful information for the preparation of PVVM coatings with high performances. As a comparison, PVVM/silica composites derived from solution blending were also prepared.

In the composite films obtained from *in situ* polymerization, the PVVM/silica nanocomposites could be well dispersed in the PVVM matrix. However, in the films derived from solution blending, the silica particles tended to agglomerate because the high viscosity of the polymer solution interfered with the dispersal of silica particles. The uniform dispersion of silica particles in the films derived from *in situ* polymerization resulted in a higher solution viscosity and better mechanical properties than those of the films obtained from solution blending.

The thermal stability, $T_g$, tensile strength, Young's modulus, impact strength, and adhesive capacity were significantly enhanced by the incorporation of silica through *in situ* polymerization. The enhancement is believed to be correlated to the extent of the dispersion of silica particles in the PVVM matrix and to the interaction between the PVVM chains and the surfaces of the silica particles. However, the addition of excessive silica particles could have resulted in the agglomeration. As a result, this lead to the deterioration of the mechanical properties.

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