

Phase-Separation Prevention and Performance Improvement of Poly(vinyl acetate)/TEOS Hybrid Using Modified Sol-Gel Process

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ABSTRACT: The formation of covalent bonds between silanols in copolymer and those in silica prevents organic–inorganic phase separation. Two series of hybrid composite materials, poly(vinyl acetate-co-vinyl trimethoxysilane)/TEOS and poly[vinyl acetate-co-3-(trimethoxysilyl)propyl methacrylate]/TEOS, were fabricated using a modified sol-gel process. The hybrids were transparent. Two kinds of silane coupling agents, vinyl trimethoxysilane (VTS) and 3-(trimethoxysilyl)propyl methacrylate (γ -MPS), were used to prevent macrophase separation through formation of covalent bonds. Thermal analysis showed that γ -MPS was more effective than VTS for the formation of covalent bonds. Enhancement of thermal stability of the hybrids was investigated by thermogravimetric analysis. Photomicrographs of scanning electron microscopy and images of atomic force microscopy indicated that inorganic silica particles were homogeneously dispersed in less than 50 nm in organic matrix. The morphological properties of hybrids were strongly dependent on the organic–inorganic composition. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2310–2318, 2001

Keywords: poly(vinyl acetate); phase-separation prevention; silane coupling agents; modified sol-gel process

INTRODUCTION

The preparation of organic–inorganic hybrid materials by the sol-gel process has drawn great attention. These materials constitute an interesting field of research. This class of materials encompasses inorganic solid as fillers in organic polymers, as well as organic moieties included in

inorganic networks.^{1–4} The sol-gel process is of interest because of its mild processing conditions such as low temperature and pressure. Starting from metal alkoxides, the inorganic network is obtained via the hydrolysis and condensation reactions.

Various kinds of organic–inorganic hybrids have been fabricated by incorporating inorganic components such as silica and titania into organic matrix by weak interaction or strong chemical bond.^{5–9} Chujo et al.^{10,11} reported the hybrids that have weak interaction at the organic–inorganic interface. To prepare these kinds of hybrids, organic polymers must have functional groups

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that can form hydrogen bonds at the interface. Meanwhile, the existence of strong covalent bonds between the organic and inorganic phases results in a reduced tendency of phase separation. Wei et al.¹²⁻¹⁴ investigated the hybrids containing covalent bonds for biomedical application. To introduce strong covalent bonds between organic and inorganic phases, vinyl monomers that have trialkoxysilyl groups have been widely used. Because these silane coupling agents have three terminal alkoxy groups, those terminal groups can form covalent bonds with silanol groups on the inorganic phase in the sol-gel reaction.

In this work, poly(vinyl acetate), which is a representative amorphous polymer, was used to prepare polymer-silica hybrids. Poly(vinyl acetate) is soft and shows excessive cold flow.¹⁵ Accordingly, it has been successfully used in paints, as adhesives for wood, and as sizing materials.¹⁶⁻¹⁸ Coltraine et al.¹⁹⁻²¹ conducted several investigations of the PVAc/TEOS hybrid systems. Silane coupling agents have been widely employed to promote adhesion in the interfaces of bulk composites.²² In this study, commercially important silanes, vinyl trimethoxysilane (VTS) and 3-(trimethoxysilyl)propyl methacrylate (γ -MPS), were used. In the sol-gel process, they were used to introduce covalent bonds between organic polymers and inorganic components. Therefore, for the preparation of poly(vinyl acetate)/TEOS hybrids, the combination of advantageous properties of polymer and silane coupling agent through copolymerization can provide macrophase separation prevention, adhesion promotion at the organic-inorganic interface, and improvement of thermal properties of the resulting hybrids. Consequently, two series of hybrid composites, poly(vinyl acetate-co-vinyl trimethoxysilane)/TEOS and poly[vinyl acetate-co-3-(trimethoxysilyl)propyl methacrylate]/TEOS, were fabricated using a modified sol-gel process in this study. These silane-modified poly(vinyl acetate)/TEOS hybrids are deemed to have a better capability of promoting adhesion and enhanced thermal and optical properties; thus, they can be applied to thin-layer coating or adhesives.

Usually in the sol-gel process, the precipitated copolymer was dried and resolved in solvent. Then the TEOS solution was added to the copolymer solution. In this work, to prevent prehydrolysis and condensation of silanes in copolymer, which might occur during precipitation of copolymer, a modified sol-gel method was employed. This method consists of separate polymerization and gelation steps. The overall process was simplified by omitting the precipitation of copolymers

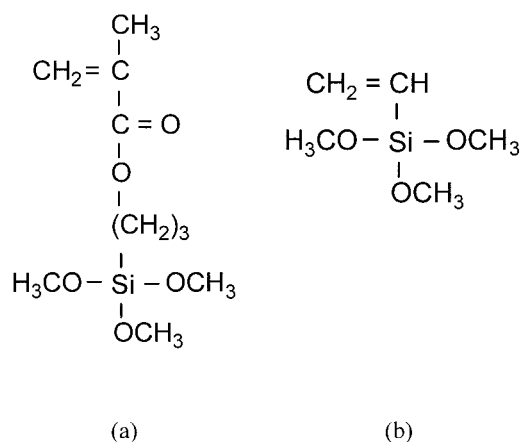


Figure 1 Chemical structures of monomeric silanes: (a) γ -MPS; (b) VTS.

and made it possible to prepare hybrid in one solution. Using this method, it was possible to efficiently introduce covalent bonds between organic polymer and inorganic silica during gelation. Moreover, it was also possible to improve the thermal, mechanical, and morphological properties by controlling the processing conditions.

EXPERIMENTAL

Materials

Vinyl acetate (VAc; Aldrich, Milwaukee, WI) was washed with 0.03M NaOH aqueous solution and distilled water to remove inhibitors, dried over anhydrous calcium chloride, and distilled under a reduced pressure. Vinyl trimethoxysilane (VTS, Aldrich), 3-(trimethoxysilyl)propyl methacrylate (γ -MPS; Dow Corning, Midland, MI), and the inorganic precursor tetraethyl orthosilicate (TEOS, Acros, New Jersey, USA) were used as received. Azobisisobutyronitrile (AIBN, Merck, Darmstadt, Germany) was recrystallized from ethanol. Tetrahydrofuran (THF, Daejung, South Korea) was dried by a common method. The structures of monomeric silanes are presented in Figure 1.

Preparation of Copolymer Precursors

Copolymerization of VAc and silane was carried out as follows. First, 0.45 mol of VAc, 0.05 mol of silane, and 0.05 g of AIBN were dissolved in 100 mL of THF. Then, the mixture was heated and stirred at the reflux temperature of THF (60°C) for 24 h. A 1-mL aliquot of copolymer solution was precipitated in *n*-hexane to determine the weight

of copolymer in 1 mL of copolymer solution. The resulting solid was dried in a vacuum oven for 12 h, after which the weight of the solid was measured. For copolymerization of VAc and VTS, 0.07 g of poly(VAc-co-VTS) was formed in 1 mL of copolymer solution. For VAc and γ -MPS, 0.15 g of poly(VAc-co- γ -MPS) was synthesized. Copolymer synthesized from 90 mol % of monomeric VAc and 10 mol % of monomeric γ -MPS was designated as PMPS1 and copolymer from 90 mol % of monomeric VAc and 10 mol % of monomeric VTS was designated as PVTS1. Other copolymers were designated as mentioned earlier.

Fabrication of Hybrid Composites

To fabricate poly(VAc-co-VTS)/TEOS hybrid composite, 7.1 mL of copolymer solution was diluted with additional THF to yield 10 mL of solution; that is, the solution contained 0.5 g of copolymer. To prepare hybrids containing organic matrix, a mixture of 2 mL of TEOS, aqueous hydrochloric acid, and distilled water in 10 mL of THF was added directly to the copolymer solution to prevent condensation of silanes in copolymer. To prepare hybrids containing inorganic matrix, 7 mL of TEOS with acid and water was added to the copolymer solution. The pH of the resulting mixture was 3. The mixture was stirred for 5 h and then cast on a petri dish and dried for 2 weeks at room temperature. To prepare poly(VAc-co- γ -MPS)/TEOS hybrid composite, 3.1 mL of copolymer solution was diluted with additional THF to make 10 mL of copolymer solution. The same mixture was poured into the copolymer solution. The sub-

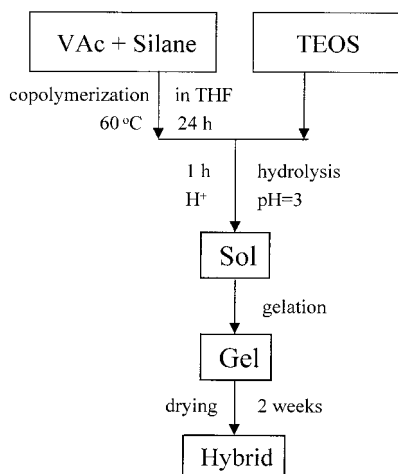


Figure 2 Schematic diagram of the modified preparation method.

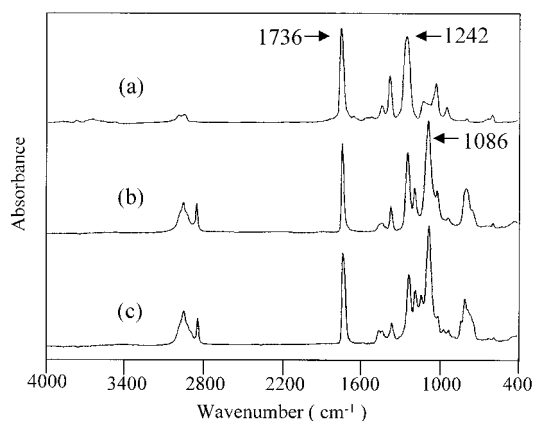


Figure 3 FTIR spectra of PVAc and copolymers: (a) PVAc; (b) poly(VAc-co-VTS); (c) poly(VAc-co- γ -MPS).

sequent procedures were mentioned earlier. The theoretical contents of organic polymers in resulting hybrids was 50 wt %. The modified preparation method is shown in Figure 2.

Instrumental Analysis

Infrared spectra were recorded on a Bomem MB 100 Fourier transform infrared (FT-IR, Canada) spectrometer. The molecular weights of copolymers were measured by Viscotek gel permeation chromatograph (GPC, Houston, Texas) using THF solvent. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C/min in N_2 . The morphology of hybrid composites was examined by a JEOL JSM 840A scanning electron microscope (SEM; JEOL, Peabody, MA). Images of fracture surfaces were taken with a Digital Instruments Dimension 3100 atomic force microscope (AFM; Digital Instruments, Santa Barbara, CA) in the tapping mode with TESP nanoprobe tips. Hardness was measured using a Barber-Colman impressor.

RESULTS AND DISCUSSION

FTIR spectra of poly(vinyl acetate) (PVAc), poly(VAc-co-VTS) (PVTS), and poly(VAc-co- γ -MPS) (PMPS) are shown in Figure 3. On the spectra of copolymers, the characteristic peak of VTS and γ -MPS observed at 1086 cm^{-1} was attributed to the asymmetric stretching of Si—O—C in Si(OCH₃). The characteristic vibrational bands of PVAc were observed at 1736 cm^{-1} for carbonyl stretching and at 1242 cm^{-1} for C—O stretching

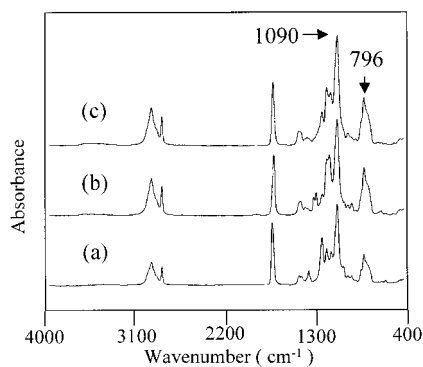


Figure 4 FTIR spectra of copolymers: (a) PMPS1; (b) PMPS2; (c) PMPS3.

on the spectra of PVAc and copolymers. No peaks for OH stretching from silanols appeared near 3400 cm^{-1} . In addition, the peaks for alkene near 1620 cm^{-1} were not shown in the spectra of copolymers. This means that the VTS and γ -MPS in copolymers retained terminal alkoxy groups. Judging from these spectra, it is believed that copolymers were synthesized without hydrolysis of monomeric silanes. In the modified sol-gel process, synthesized copolymers were used without precipitation. Therefore, the process could be simplified without loss of advantageous properties of the resulting hybrids.

FTIR spectra of copolymers are presented in Figures 4 and 5. As the composition of monomeric silane was increased, the absorption intensity of the peak at 796 cm^{-1} for Si—OMe symmetric stretching was increased. The absorption intensity of the peak at 1090 cm^{-1} for Si—OMe asymmetric stretching was also increased. This implies that the composition of the silane units in synthesized copolymer was increased.

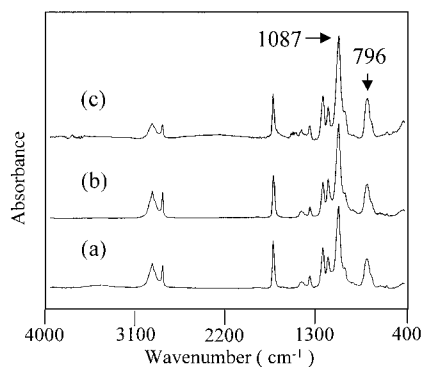


Figure 5 FTIR spectra of copolymers: (a) PVTS1; (b) PVTS2; (c) PVTS3.

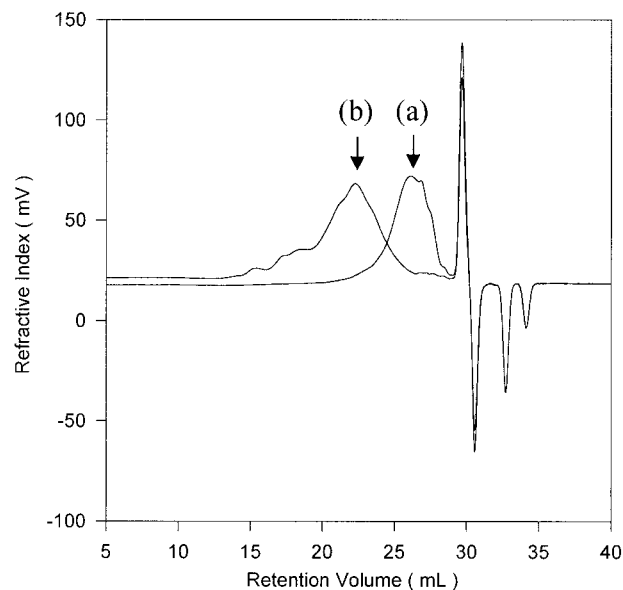


Figure 6 Gel permeation chromatograms of copolymers: (a) PVTS1; (b) PMPS1.

The gel permeation chromatograms of copolymers obtained after drying of solvent are presented in Figure 6. The weight-average molecular weights of copolymers are summarized in Table I. Because the precipitation of copolymer was not conducted during the sol-gel process, oligomers should be contained in the copolymer solutions. Although the chromatograms were broad, peaks for low-molecular oligomers near the peaks for solvent were not clearly observed. This means the effect of oligomers on the organic-inorganic composition of hybrids was not significant. γ -MPS has a bulky pendant group and the pendant group has a tendency to donate an electron to the double bond. Although the alkene of γ -MPS is sterically more hindered than that of VTS, the donated electron on the double bond of γ -MPS makes it more reactive toward polymerization. Therefore, the alkenes of γ -MPS are likely to be attacked by

Table I Weight-Average Molecular Weight of Copolymers

Copolymer	M_w
PMPS1	100,000
PMPS2	81,000
PMPS3	73,000
PVTS1	50,000
PVTS2	42,000
PVTS3	38,000

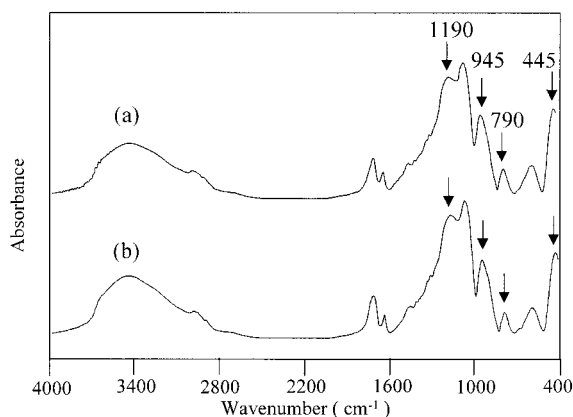


Figure 7 FTIR spectra of two prepared hybrids: (a) PVTS1/TEOS; (b) PMPS1/TEOS.

radical more easily than those of VTs. That is the reason the molecular weight of PMPS is higher than that of PVTS.

Figure 7 exhibits the FTIR spectra of the fabricated hybrids PVTS1/TEOS and PMPS1/TEOS. From the figure, the characteristic vibrational bands of silica are shown at 1190, 940, 790, and 450 cm^{-1} , the assignments of which are presented in Table II. The spectra showed that silica was incorporated into polymer matrix, which means that the hybrids were prepared successfully.

Figure 8 shows TGA thermograms of hybrids. A major weight loss was observed at elevated temperature because of the thermal decomposition of organic polymer. PVAc/TEOS began to lose weight at 300°C. However, the initial decomposition temperatures of PVTS1/TEOS and PMPS1/TEOS were significantly higher than that of PVAc/TEOS. The increase of thermal decomposition temperature was ascribed to a strong interaction such as covalent bonding. The thermal decomposition of copolymer was retarded by the covalent bonds between copolymer and silica. Consequently, it can be inferred that the thermal stability of the silane-modified hybrid was enhanced.

Table II Vibrational Bands of Silica and Their Assignments

ν/cm^{-1}	Assignment
1630	Si—OH deformation on the silica surface
1190	Si—O—Si asymmetric stretching
945	Si—O stretching from silanol
790	Si—O—Si symmetric stretching
445	Si—O—Si bending

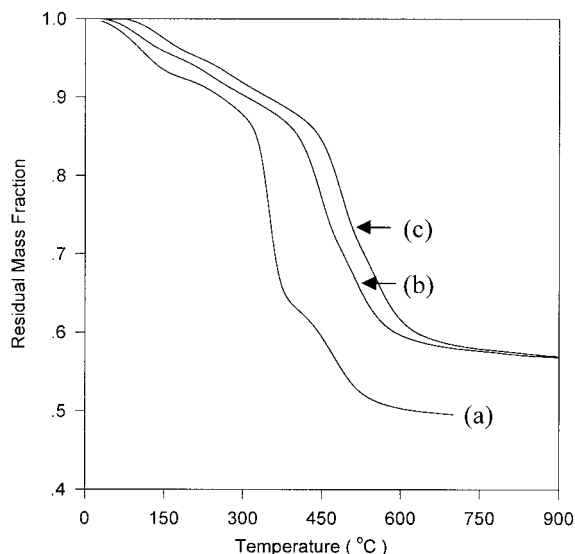


Figure 8 TGA curves of hybrid composites: (a) PVAc/TEOS; (b) PVTS1/TEOS; (c) PMPS1/TEOS.

To examine the difference in thermal resistivity between PMPS1 and PVTS1 in hybrids, differential TG curves of PVTS1/TEOS and PMPS1/TEOS are exhibited in Figure 9. There were two distinct weight losses. The first weight loss at around 350 and 400°C was considered to reflect the decomposition of organic copolymers PVTS1 and PMPS1, respectively. The decomposition temperature of PMPS1 was higher than that of PVTS1. This means that γ -MPS is also effective

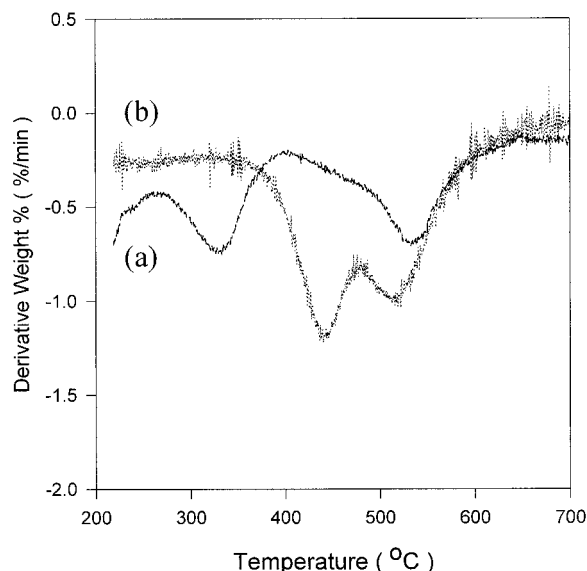


Figure 9 Differential TG curves of silane-modified hybrids: (a) PVTS1/TEOS; (b) PMPS1/TEOS.

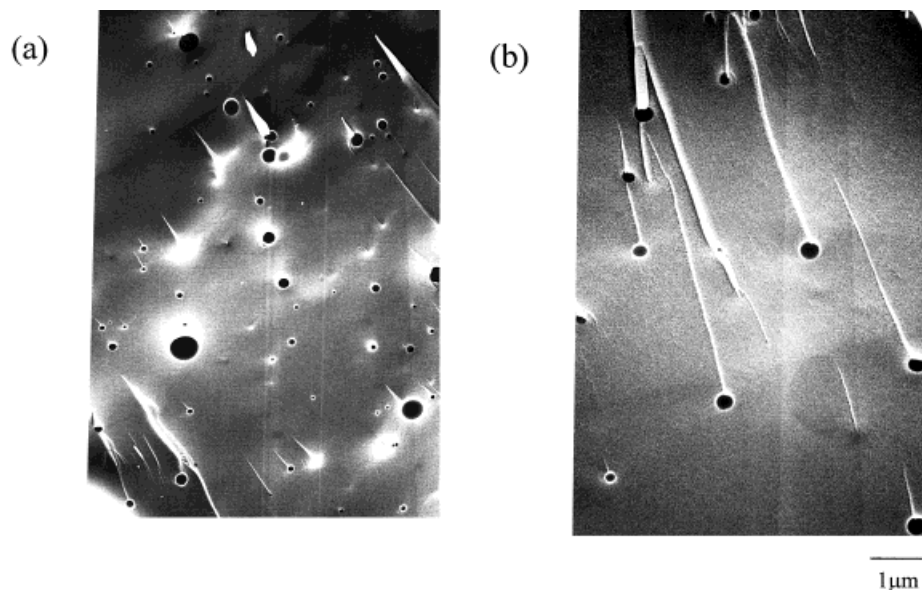


Figure 10 SEM photographs of fracture surfaces of hybrids thermally treated at 700°C for 6 h: (a) PVTS1/TEOS; (b) PMPS1/TEOS.

for enhancing thermal stability by efficiently forming covalent bonds. MPS has a long and flexible pendant group, which can make MPS interact efficiently with the inorganic component. Therefore, PMPS1/TEOS should have a more stable structure than PVTS1/TEOS.

Figure 10 shows the photographs of fracture surfaces of thermally treated PVTS1/TEOS and PMPS1/TEOS. Many pores on the fracture surfaces of thermally treated hybrids were formed as a result of thermal decomposition of organic copolymers. Pore sizes were less than 300 nm, which means that the domain sizes of the organic component in the hybrid were less than 300 nm. Therefore, the hybrids were transparent to visible light. Comparing photographs (a) and (b) of Figure 10, more pores were observed on (a). The pores reflected the sites at which thermal decomposition occurred during thermal treatment, which means that the thermal decomposition of PVTS1 in the hybrid occurred more easily than the decomposition of PMPS1. This result shows a good agreement with thermal analysis.

The morphological features of the hybrids were probed by atomic force microscopy. AFM images of the fracture surfaces of the hybrids are presented in Figure 11. The images show that inorganic particles are homogeneously dispersed in the organic matrix. Height images show that the average sizes of the silica particles in the hybrids are less than 50 nm. The hybrids were transpar-

ent to visible light. The features illustrate that the fabricated hybrids were nanohybrids. It was hard to detect the macrophase separation just from the images of surfaces of hybrids. Even though each image might reflect the surface roughness of each hybrid, phase images confirm the homogeneous incorporation of inorganic silica into the polymer matrix in nanoscale.

As described earlier, it was possible to improve the performance of hybrids by controlling two factors, the VAc-to-silane ratio and copolymer-TEOS composition. The enhancement of thermal stability measured by TGA is presented in Table III. As the composition of silane in copolymer synthesis was increased, the thermal decomposition temperature of the organic component in the hybrid was increased. As the composition of monomeric silane was increased, the number of silane units in the synthesized copolymer was also increased. Accordingly, this fact implies that more silane units induced the efficient formation of covalent bonds at the organic-inorganic interface. Similarly, the residual weight of the hybrid was increased. Given that the same amount of inorganic precursor was used for the preparation of hybrids, the increase of residual mass was attributed to the formation of a silica network from condensation between silanol in hydrolyzed silane in copolymer and that in inorganic silica.

As the composition of monomeric silane was increased, the hardness of the hybrid was in-

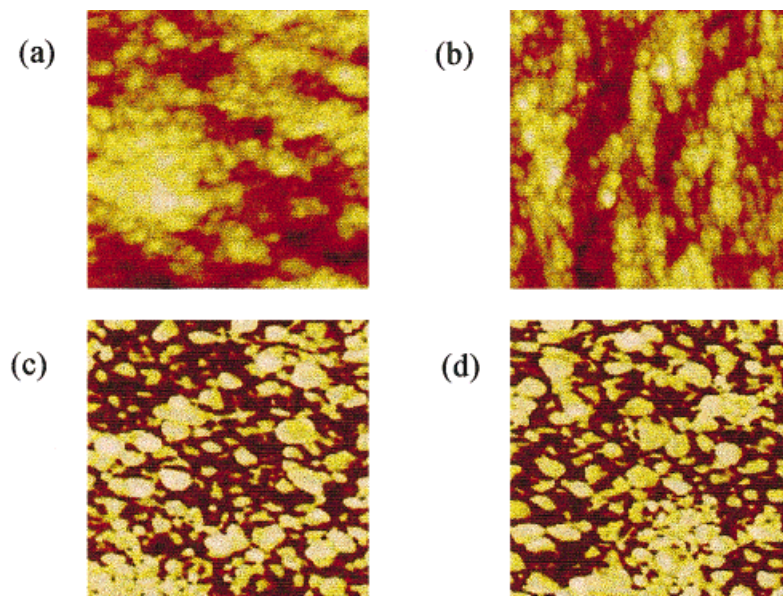


Figure 11 AFM images of fracture surfaces of hybrids (500×500 nm): (a) height image of PVTS1/TEOS; (b) height image of PMPS1/TEOS; (c) phase image of PVTS1/TEOS; (d) phase image of PMPS1/TEOS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

creased, as Figure 12 indicates. Although the hybrids had the same amount of silica, the hardnesses were quite different, which means that the effect of silica content on the hardness of hybrid was not significant. Even though γ -MPS and VTS have different structures, the tendencies of the increase in hardness were similar. The increase in hardness could be attributed to the strong interfacial interaction. These results could be an indirect evidence of the formation of a covalent bond between the organic phase and the inorganic phase. As shown in Table III and Figure 12, it was possible to improve thermal and mechanical prop-

erties by increasing the composition of monomeric silanes in the copolymerization step.

Morphological features of prepared hybrids are exhibited in Figures 13 and 14. The images show that inorganic silica is homogeneously dispersed in the organic matrix. The average sizes of the silica particles in the hybrids were less than 50 nm. The images illustrate that the fabricated hybrids are nanocomposites. The sur-

Table III Enhancement of Thermal Stability Detected by TGA

Hybrid	Residual Mass (%)	DTG ($^{\circ}\text{C}$) ^a
PVAc	—	280
PVTS1	—	296
PMPS1	—	307
PMPS1/TEOS	41.9	391
PMPS2/TEOS	46.3	412
PMPS3/TEOS	50.6	426
PVTS1/TEOS	37.5	364
PVTS2/TEOS	44.8	381
PVTS3/TEOS	49.7	393

^a Onset temperature of degradation of organic component.

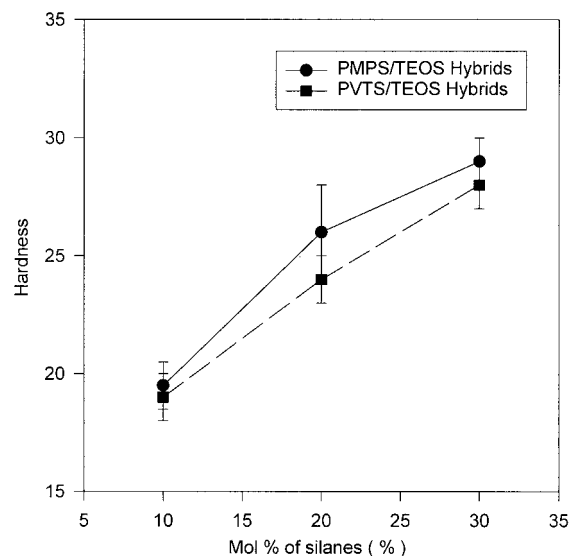


Figure 12 Surface hardness of prepared hybrids.

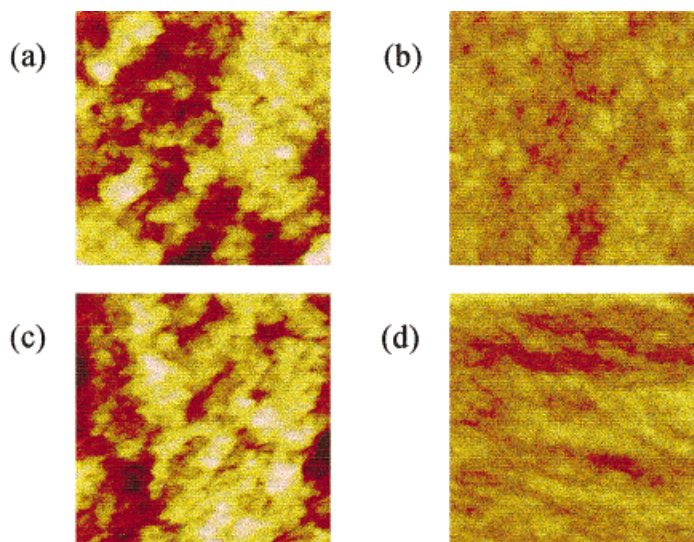


Figure 13 AFM images of fracture surfaces of hybrids (500×500 nm): (a) height image of PVTS2/TEOS containing 12.5 wt % silica; (b) height image of PVTS2/TEOS containing 50 wt % silica; (c) height image of PMPS2/TEOS containing 12.5 wt % silica; (d) height image of PMPS2/TEOS containing 50 wt % silica. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

face roughness of PMPS3/TEOS hybrid containing 50 wt % silica was smaller than that of PMPS3/TEOS containing 12.5 wt % silica. However, PMPS2/TEOS containing 12.5 wt % silica and PMPS3/TEOS containing 12.5 wt % silica had nearly the same surface roughness. VTS-

modified hybrids had similar morphological features. All the prepared hybrids did not show any apparent macrophase separation. Therefore, it was possible to prevent phase separation using only a small amount of silane, less than 10 mol % of VAc. Furthermore, the morpholog-

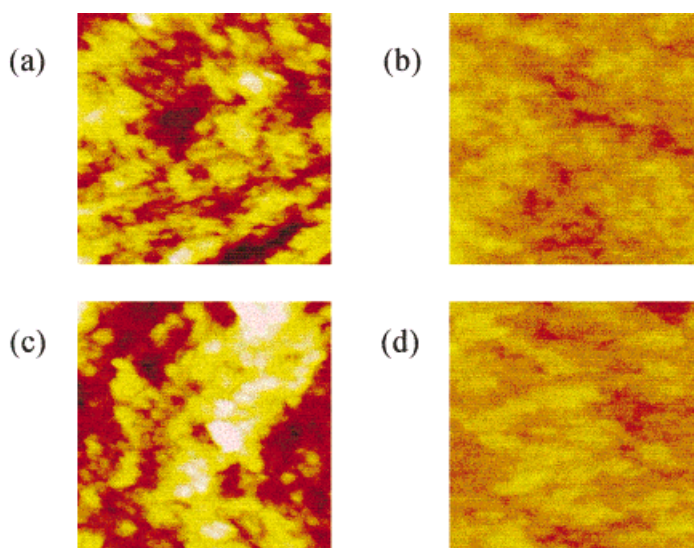


Figure 14 AFM images of fracture surfaces of hybrids (500×500 nm): (a) height image of PVTS3/TEOS containing 12.5 wt % silica; (b) height image of PVTS3/TEOS containing 50 wt % silica; (c) height image of PMPS3/TEOS containing 12.5 wt % silica; (d) height image of PMPS3/TEOS containing 50 wt % silica. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ical properties of hybrids were strongly dependent on the organic–inorganic composition. When the inorganic component was dominant in the hybrid, the surface roughness was nearly negligible. Consequently, those hybrids can be applied to coating materials.

CONCLUSIONS

In this study, two series of silane-modified PVAc/TEOS hybrids were successfully fabricated by copolymerization of VAc and silanes. In these hybrids, silica particles were homogeneously incorporated into the organic matrix using a modified sol-gel method. This method could prevent prehydrolysis and condensation of silanes in copolymers, which might occur during precipitation of copolymers. The process was simplified by omitting the precipitation of copolymers and made it possible to prepare the hybrid in one solution. Silanes in the copolymers could facilitate condensation reaction and significantly prevent macrophase separation by forming covalent bonds with the inorganic phase in the sol-gel process. Thermal analysis showed that γ -MPS was more effective than VTS for the formation of covalent bonds. It was possible to improve not only the thermal and mechanical properties by controlling the composition of silane in copolymers but also the morphological properties by controlling the organic–inorganic composition.

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