

A comparative study of grafting steps on the preparation and properties of modified nanosilica for UV-curable coatings

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Abstract Nanosilica was modified and functionalized with acrylsilane by the “grafting to” method via different grafting steps, i.e., prepared-grafting step and step-wise propagation. The prepared-grafting step was achieved by grafting the nanosilica surface with the prepared acrylsilane, which was obtained by thiol-ene click reaction between 3-mercaptopropyl trimethoxysilane (MPTMS) and trimethylolpropane triacrylate (TMPTA). The step-wise propagation was achieved by first grafting MPTMS onto the nanosilica surface and then using the mercapto groups as initiators to react with TMPTA. The acrylsilane was characterized by FTIR. The modified nanosilica was characterized by FTIR, TGA, and contact angle analysis. It was demonstrated that the thiol-ene click reaction can easily occur between MPTMS and TMPTA. The grafting ratio of modified nanosilica via prepared-grafting step was higher than that of step-wise propagation. The SEM images of fractured films containing modified nanosilica also indicated that the former is more effective than the latter in reducing the self-aggregation of nanosilica. The effects of modified nanosilica on the viscosity and hardness of UV-curable coatings were also investigated.

Keywords Surface modification, Nanosilica, Grafting to, UV-curable coatings, Acrylsilane

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Introduction

In recent years, polymer/nanosilica composites have found wide application not only in scientific fields, but also in various industrial products.^{1,2} However, it seems to be difficult to obtain well-dispersed polymer/nanosilica hybrids owing to the strong tendency of aggregation among the nanosilica and polymer.^{3–5} Consequently, it is necessary to carry out surface modification before nanosilica is used in a polymer matrix.^{6–8} Two different methods have been employed for the nanosilica surface modification. The first method is the “grafting to” method, in which the end-functionalized macromolecules are attached to the reactive hydroxyl groups of the nanosilica surface. The second method is the “grafting from” method, in which the situ monomer polymerized with monomer growth of polymer chains from the immobilized initiators step by step.^{9–12} However, there are certain advantages and limitations inherent in each of the two methods. The “grafting from” method is the most promising method in the preparation of polymer/nanosilica with higher grafting density, but the modified nanosilica usually had broad particle size distributions because the difference of the molecular weight of grafted polymer was great.¹³ While the “grafting to” method usually exhibits lower grafting density, the processing is simple. To the best of our knowledge, the reactive groups used in the “grafting from” method were usually achieved by the “grafting to” method.^{9,14} Therefore, the “grafting to” method is basic and universal, in which the polymers can be easily attached onto the nanosilica surface either by directly grafting available polymer onto the nanosilica surface (prepared-grafting step) or by forming the polymer chains via step-wise propagation with the grafted reactive groups. However, most previous research has focused on the influences of different grafting methods (“grafting from” and “grafting to”) on the properties of final

hybrids. Few reports have been found about the effects of different grafting steps (prepared-grafting step and step-wise propagation) in the “grafting to” method on the final properties of hybrids.^{9,14}

In comparison with the polymer, the monomers usually have a low molecular weight; they can penetrate the aggregated nanosilica and react with the hydroxyl groups on the nanosilica surface. As a result, the nanosilica used in UV-curable coatings is always modified by grafting suitable acrylsilane onto the nanosilica surface.¹⁵ The miscibility of nanosilica and the organic coating, the mechanical properties, and the thermal stability of organic coatings are significantly improved.^{15–18} In addition, the existing vinyl groups grafted onto nanosilica can crosslink with the acrylate matrix. However, the grafted acrylsilanes are usually monofunctional because the most available acrylsilane is monofunctional. In our previous work, we obtained modified nanosilica with multiple functional acrylate groups by first grafting 3-aminopropyl triethoxysilane and then grafting multiple functional acrylate via Michael reaction between amino groups and vinyl groups.¹⁹ In recent years, the mild reaction conditions of the thiol-ene click reactions provide more feasibility for grafting multiple functional acrylsilanes^{20–22} and polymer^{23–26} onto the nanosilica surface in UV-curable coatings.

In this study, the “grafting to” method was used to modify nanosilica with the multiple functional acrylsilane, which was obtained via thiol-ene click reaction between 3-mercaptopropyl trimethoxysilane (MPTMS) and trimethylolpropane triacrylate (TMPTA). The differences between the prepared-grafting step and step-wise propagation were compared. The influences of grafting steps on the grafting efficiency, particle size, and dispersion of modified nanosilica were investigated. The effects of modified nanosilica prepared via different steps on the properties of UV-curable coatings were also studied and compared.

Experimental

Materials

Nanosilica powder (SP1) with an average particle size of 20–50 nm and silanol group content of 1.9 mmol/g was obtained from Zhejiang Hongcheng Materials Co., China. MPTMS was purchased from Sigma Chemical Co. Epoxy acrylate (EA) with double functionality, tripropylene glycol diacrylate (TPGDA), and TMPTA were provided by UCB Chemicals. 2,4,6-Trimethylbenzoyl diphenylphosphine oxide (TPO) from Ciba-Geigy was used as photoinitiator. All other chemicals were analytical pure reagents (AR). Nanosilica was kept in a vacuum chamber for 24 h at 100°C and the other materials were used without further purification.

Grafting acrylsilane to nanosilica surface via prepared-grafting step

The prepared-grafting step included two independent steps. The first step was the preparation of acrylsilane, which was obtained as follows: 118.6 g TMPTA (0.4 mol) and 0.2 g *p*-hydroxyanisole were added into a 500 mL four-neck flask equipped with a mechanical stirrer and thermometer, 79.3 g MPTMS (0.4 mol) and 0.2 g triphenylphosphine were dropped into the flask within 30 min, and the mixture was stirred at room temperature and irradiated by UV light with the main wave length of 365 nm. The reaction process was determined by the variation of integrated area of the peak in the range of 1533–1673 cm⁻¹ corresponding to acrylate double bonds in FTIR spectra. After the conversion of acrylate double bonds reached about one-third, the viscous transparent fluid was obtained and abbreviated as AC-silane.

The second step was the modification of nanosilica. 10 g nanosilica was dispersed in 150 mL anhydrous toluene under mechanical stirring and ultrasonic dispersing for 30 min. The mixture was stirred at 300 rpm for a further 1 h, and then another prepared mixture consisting of 10 mL water, 10 mL anhydrous ethanol, 2 mL formic acid, and 197.9 g AC-silane were added under vigorous stirring. After continuously stirring for 4 h at the reflux temperature, the obtained suspension was separated by centrifugation. After filtration and extraction with toluene for 12 h to remove the excess silane physically adsorbed on the nanosilica, the modified nanosilica was dried in a vacuum at 90°C for 24 h. Then modified nanosilica with acrylsilane via prepared-grafting step was obtained and called PG-silica.

Grafting acrylsilane to the nanosilica surface via step-wise propagation

First, the MPTMS was grafted onto the nanosilica surface according to the above method of grafting AC-silane. The highest grafting ratio, which is more helpful to the further grafting, was obtained with 10 g nanosilica and 79.3 g (about 75 mL) MPTMS according to our previous research result.²⁷ Then 10 g modified nanosilica and 118.6 g TMPTA were agitated at room temperature and irradiated by UV light with the main wavelength of 365 nm. After 20 h, unreacted TMPTA was removed by extracting with toluene for 12 h. The product was dried in a vacuum at 90°C for 24 h. Then modified nanosilica with acrylsilane via step-wise propagation was obtained and called SW-silica.

Preparation of UV-curable coatings

The UV-curable coatings in this study were a mixture of 30 wt% EA, 40 wt% TPGDA, 25 wt% TMPTA, and 5 wt% TPO. The nanosilica and modified nanosilica

were directly added into the above mixture with different levels, and then dispersed by ultrasonic irradiating for 1 h at room temperature. Finally, the different hybrid coatings were obtained.

Characterizations and measurements

Samples were analyzed by a Nicolet 360 FTIR spectrometer (USA). Solid samples were ground with KBr and compressed into pellets; liquid samples were coated on the KBr pallets. FTIR spectra were recorded in the 400–4000 cm^{-1} range with 16 scans.

The percentage conversion of acrylate groups in thiol-ene click reaction was detected by FTIR. The conversions were estimated from the variation of integrated area in the range of 1533–1673 cm^{-1} corresponding to the acrylate double bonds, and the carbonyl group absorption peak in the range of 1688–1828 cm^{-1} was used as the internal standard. At a subsequent time t , the area of the peak can be integrated and the conversion at the reaction time can be determined according to our previous methods as follows²⁸:

$$\text{Conversion}(\%) = \frac{A_{0(\text{C}=\text{C})}/A_{0(\text{C}=\text{O})} - A_{t(\text{C}=\text{C})}/A_{t(\text{C}=\text{O})}}{A_{0(\text{C}=\text{C})}/A_{0(\text{C}=\text{O})}},$$

where $A_{0(\text{C}=\text{C})}$ and $A_{t(\text{C}=\text{C})}$ are the integrated area of acrylate double bonds in the range of 1533–1673 cm^{-1} at the initial time and the time t , respectively. Meanwhile, $A_{0(\text{C}=\text{O})}$ and $A_{t(\text{C}=\text{O})}$ are the integrated area of carbonyl group absorption peak in the range of 1688–1828 cm^{-1} at the initial time and the time t , respectively.

The Agilent 1100 HPLC system equipped with a quaternary pump, an autosampler with variable injection capacity from 0.1 to 100 μL , and a UV detector, was used to analyze the AC-silane. The mobile phase was the mixture of water and acetonitrile with volume ratio of 1:4, and the UV wavelength was set at 254 nm. The sample injection volume was 1.0 μL .²⁹

The thermogravimetric analysis (TGA) was performed in a HCT-1 thermal gravimetric analyzer (Henvan Scientific Instrument Co., China) under an air atmosphere from room temperature to 700°C with heating rate of 20°C/min and air flow speed of 50 mL/min. The grafting ratio (R_g) was calculated according to the following equation³⁰:

$$R_g = \left(\frac{W_1}{W_1} - \frac{W_0}{W_0} \right) \times 100\%,$$

where W_1 is the starting weight of the modified nanosilica particles, W_1 is the residual weight of the modified nanosilica particles at 700°C, W_0 is the starting weight of unmodified nanosilica particles, and

W_0 is the residual weight of unmodified nanosilica particles at 700°C.

The water contact angles (CAs) were measured with deionized water drops on the nanosilica surface pellets, which were obtained by compacting nanosilica powder with 100 kN force. The measurement was carried out within 10 s by a Krüss CA instrument (Easydrop DSA 20) at room temperature using the sessile drop fitting method for the static CA. For each sample, at least five measurements were made, and the average was taken.

The viscosities of coatings were measured by a NDJ-79 rotation viscometer (Shanghai Scientific Instrument Co., China) at 25°C.

The morphology of UV-curable film containing modified nanosilica was visualized by JEOL JSM-6700F field-emission scanning electron microscopy (FE-SEM). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of ~ 30 nm.

To measure the hardness of UV-curable films, the coatings with a wet thickness of 100 ± 5 μm were applied on aluminum plates and then processed by being exposed to a medium pressure Hg lamp (1 kW, 80 W/cm^2) for 2 min and being put in a dark place for 5 h. The Shore D hardness was determined according to the testing method of ASTM D2240.

Results and discussion

Preparation and characterization of acrylsilane

In order to graft the multiple functional acrylsilane onto the nanosilica surface, the acrylsilane is first synthesized via thiol-ene click reaction between MPTMS and TMPTA. Containing mercapto groups, the MPTMS can react quantitatively with acrylate groups of TMPTA by thiol-ene click reaction under the UV light irradiation.

There are three acrylate functionalities, which react with monothiol functionality in the thiol-ene click reaction. The side reaction is inevitable; two measures were used to obtain the designed product with higher yield. First, the temperature was controlled at room temperature, and *p*-hydroxyanisole was used as inhibitor in order to prevent polymerization of TMPTA. Second, the MPTMS was dropped into the TMPTA, which ensured the acrylate groups are in excess over thiol, therefore, adding MPTMS will first react with TMPTA, rather than TMPTA–MPTMS adduct, because of steric hindrance. The reaction scheme is selected and represented in Fig. 1.

The click reaction between MPTMS and TMPTA can be monitored by the variation of characteristic absorption peak in FTIR. Theoretically, the absorption peak of acrylate groups and mercapto groups will decrease progressively with the reaction time increasing, and the reaction is thought to be finished until the mercapto group disappeared or the related integrated

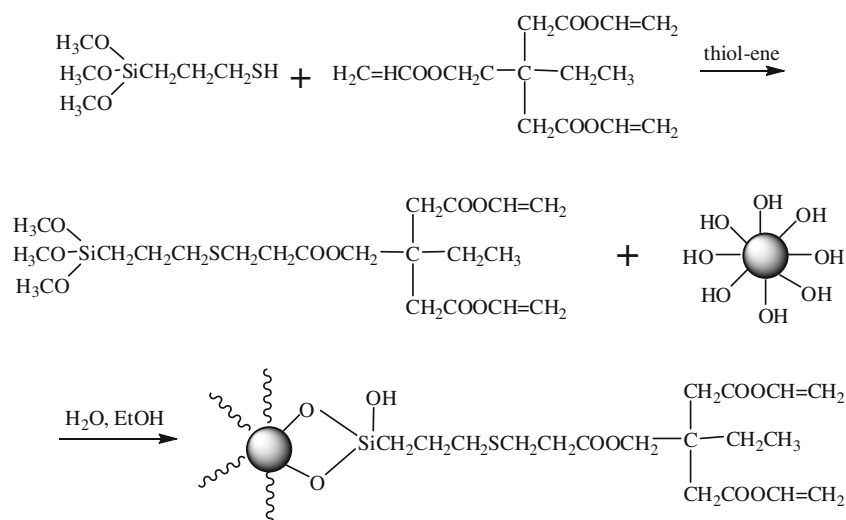


Fig. 1: Preparation and grafting of acrylsilane onto the nanosilica surface via prepared-grafting step

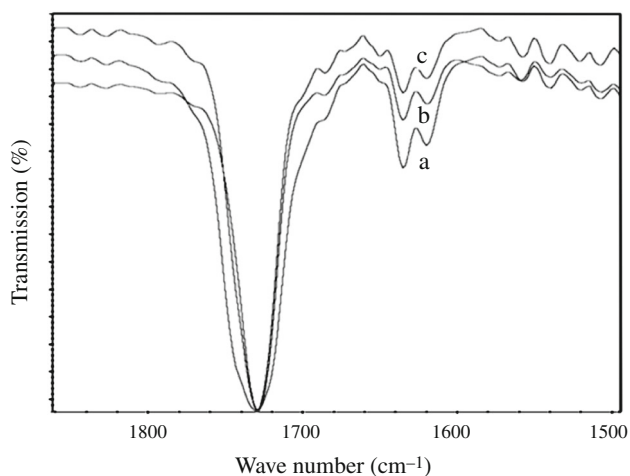


Fig. 2: The characteristic absorption peak variation of addition product between MPTMS and TMPTA with time of (a) 0 h, (b) 2 h, and (c) 5 h

area of acrylate groups decreased one-thirds. However, the characteristic peak of mercapto groups at 2570 cm^{-1} in FTIR is very weak and the variation is not easy to detect, therefore, the acrylate groups at 1635 cm^{-1} are used to detect the reaction progress.

In Fig. 2, the mixture of MPTMS and TMPTA showed the characteristic absorption peaks of $-\text{CH}=\text{CH}_2$ group at 1635 cm^{-1} and $-\text{C}=\text{O}$ group at 1730 cm^{-1} . Increasing reaction time led to the decrease in the intensity of the acrylate group peak progressively. After 5 h, the conversion of acrylate double bonds reached about one-third. The mercapto group was not detected in the final product, according to the method of reference.³¹ It can be concluded that thiol-ene click reaction between MPTMS and TMPTA had occurred.

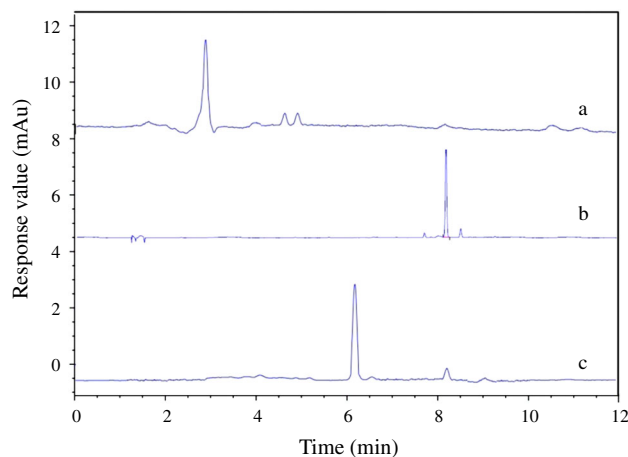


Fig. 3: Liquid chromatography of (a) MPTMS, (b) TMPTA, and (c) final product

The obtained product may be a mixture of TMPTA–MPTMS, TMPTA–2MPTMS, and TMPTA–3MPTMS with the mole ratio of TMPTA and MPTMS of 1:1, 1:2, and 1:3, respectively. The TMPTA–3MPTMS cannot be easily obtained on the condition of excess TMPTA. The liquid chromatography (Fig. 3) of the final product showed that there is only one main peak, which indicated that there is only one main product. The TMPTA peak is not obvious in the final product, which proved that the main product is TMPTA–MPTMS. Otherwise, either TMPTA–2MPTMS or TMPTA–3MPTMS in the product will leave unreacted TMPTA on the above feeding ratio.

Consequently, the desired acrylsilane can be synthesized by thiol-ene click reaction between MPTMS and TMPTA according to the above synthesis scheme and reaction conditions.

The difference in preparation of modified nanosilica via different steps

Figures 1 and 4 show the difference between two different grafting steps. In the prepared-grafting step, the acrylsilane was first prepared and then grafted onto the nanosilica surface. The grafting procedure was carried out by the condensation of the silanol group of nanosilica surface and siloxane of acrylsilane. The detail process was similar to the first step of step-wise propagation, in which the MPTMS was grafted onto the nanosilica surface and the surface hydroxyl group was replaced by the mercapto group. The next step was that the mercapto group was used as a functional group to react with TMPTA for preparation of modified nanosilica. The final grafting ratio and properties of modified nanosilica rely on the first step greatly. The difference in modified nanosilica, prepared by two different grafting steps, was characterized by FTIR and TGA.

The FTIR spectra of nanosilica modification before and after are shown in Fig. 5. In the spectra of nanosilica (curve a), we can see that the stretching vibration peaks of Si–OH reaches near 3430 cm^{-1} , the asymmetric stretching vibration near 810 cm^{-1} , and the symmetric stretching vibration and bending vibration near 470 cm^{-1} of Si–O–Si.³² After grafting with an organic compound, the related strength of peak at 3430 and 1650 cm^{-1} corresponding to –OH on the nanosilica surface decreased, the carboxyl groups at 1700 cm^{-1} increased, and the methylene at 2938 and 2873 cm^{-1} were observed in the modified nanosilica, which proves that the organic compound has been successfully grafted onto the nanosilica surface. However, the appearance of a peak at 3430 cm^{-1} shows that –OH on the surface of nanosilica had not reacted completely. We can see that the absorption peak intensity of the carboxyl groups and methylene group in modified nanosilica by prepared-grafting method is stronger than that of step-wise propagation. It can be ascertained that the former is more effective in grafting acrylsilane onto the nanosilica surface.

In order to further quantitatively check out the difference between the two different grafting steps, the grafting ratio of organic materials on the nanosilica surface was determined by TGA as shown in Fig. 6,

which was performed from room temperature to 700°C with a heating rate of $20^\circ\text{C}/\text{min}$. The result shows that the unmodified nanosilica had a weight loss (about 8 wt%) before 700°C , which is related to the elimination of physically and chemically absorbed water on the surface.³³ The physically absorbed water was attributed to the weight loss up to 120°C , while chemically bound water was attributed to the weight loss from 120 to 700°C .

As for modified nanosilica, there are two significant differences in the TGA curves. The first difference is grafting ratio: the value is 143.2% for PG-silica, while the value is 21.9% for the SW-silica. The second difference is decomposition temperature. The continuous weight loss occurred from 250 to 700°C for SW-silica, which can be ascribed to the thermal decomposition of organic chains. Whereas there are two obvious stages in weight loss for PG-silica, the first weight loss from 150 to 350°C is probably attributed to the physically absorbed organic compounds and self-condensation of grafting acrylsilane. The second weight loss from 350 to 700°C can be attributed to

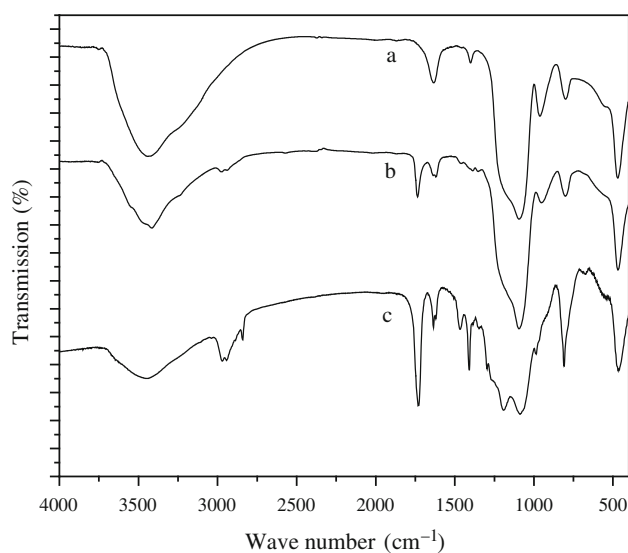


Fig. 5: The FTIR spectra of (a) nanosilica, (b) SW-silica, and (c) PG-silica

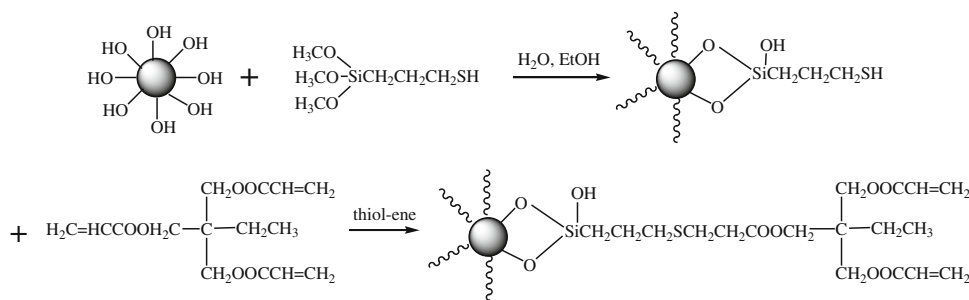


Fig. 4: Preparation and grafting of acrylsilane onto the nanosilica surface via step-wise propagation

the thermal decomposition of chemical-bonded groups on the surfaces. The TGA results are in good agreement with the FTIR spectra results, indicating that the acrylsilane segments have been bonded chemically to silica particles in both methods, and the PG-silica has a higher grafting ratio than SW-silica.

The hydrophobicity of the nanosilica modification before and after was investigated by water CA measurements. In Fig. 7, there are three different images that were taken from the Krüss software. Figures 7a, 7b, and 7c show the water drops on the surface of the nanosilica, SW-silica, and PG-silica, respectively. The results showed that the unmodified nanosilica was strongly hydrophilic. It also can be seen that the acrylsilane on the nanosilica surface resulted in a significant enhancement in water CA. However, the difference between the two different modification steps is obvious. It can be seen that the prepared-grafting is better than the step-wise propagation in increasing the hydrophobicity, which is an important factor in determining the dispersion of nanosilica in organic coatings.

There are at least two factors that can be responsible for the above phenomena. The first is that the surface functional groups, which reduced from 1.9 mmol/g hydroxyl group to 0.9 mmol/g mercapto group in

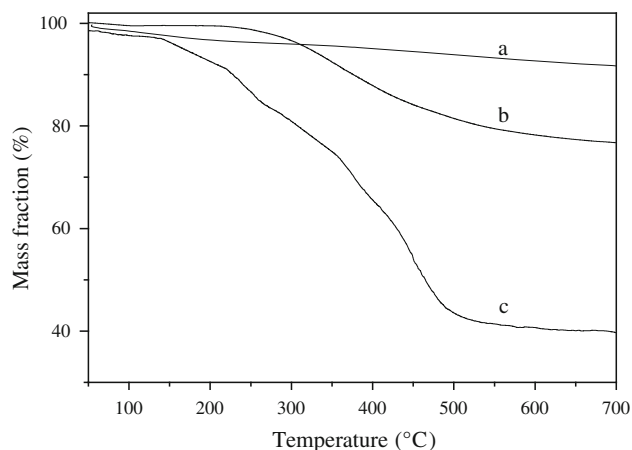


Fig. 6: The TGA curve of (a) nanosilica, (b) SW-silica, and (c) PG-silica

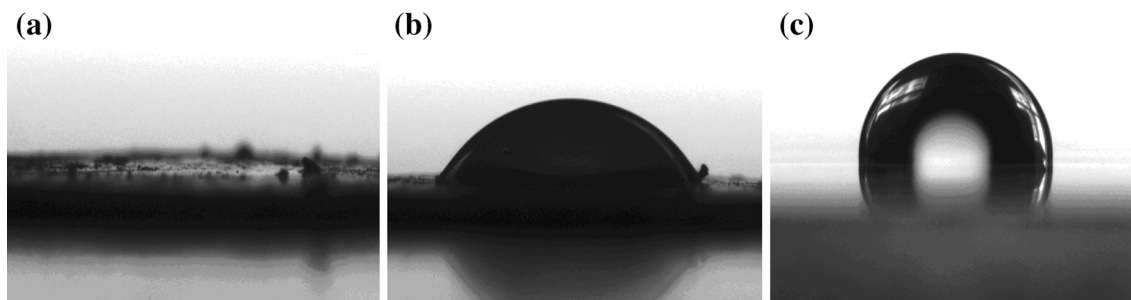


Fig. 7: The contact angle of water on the pellets of (a) nanosilica, (b) SW-silica, and (c) PG-silica

SW-silica particles,²⁷ provide less reactive groups for the following thiol-ene click reaction and lead to a lower grafting ratio. The second reason is that the grafted MPTMS will encapsulate the nanosilica, and the strong steric hindrance effect means only a few organic chains can grow from the particles in spite of the excess monomer for modified nanosilica.

The dispersion of modified nanosilica in the UV-curable coatings

The main goal of nanosilica modification is to improve the dispersion and reduce self-aggregation of nanosilica particles in organic materials. The improvement degree is determined by the organic functional groups onto the nanosilica surface and the grafting ratio.³⁴ SEM is an important method to observe the dispersion situation of inorganic particles. Figure 8 shows the fractured surface morphology of pure coatings and coatings with modified nanosilica. We can see from SEM micrographs that the pure UV coating forms films with a smooth and uniform surface without cracks. The modified nanosilica particles in the UV coating cause some particles and small cracks to be present on the fractured surface of the films, and it shows that most of the nanosilica particles remained on a nanometer in the UV cured films. SEM micrographs of the fracture surfaces of the samples containing modified nanosilica, prepared with different steps, show an obvious difference in the dispersion of nanosilica. It shows that the self-aggregation of SW-silica in UV cured films is reduced but still existed to a certain degree, while the PG-silica exhibited homogeneous dispersion in UV-curable coatings. The homogeneous dispersion of nanosilica was attributed to the higher grafting ratio of modified nanosilica.

Effect of modified nanosilica on the viscosity of UV-curable coatings

The viscosity of a UV-curable system, which affects the processability and the photopolymerization rate of the cured film, is considered to be one of the most important parameters.³⁵ The viscosities of the UV-

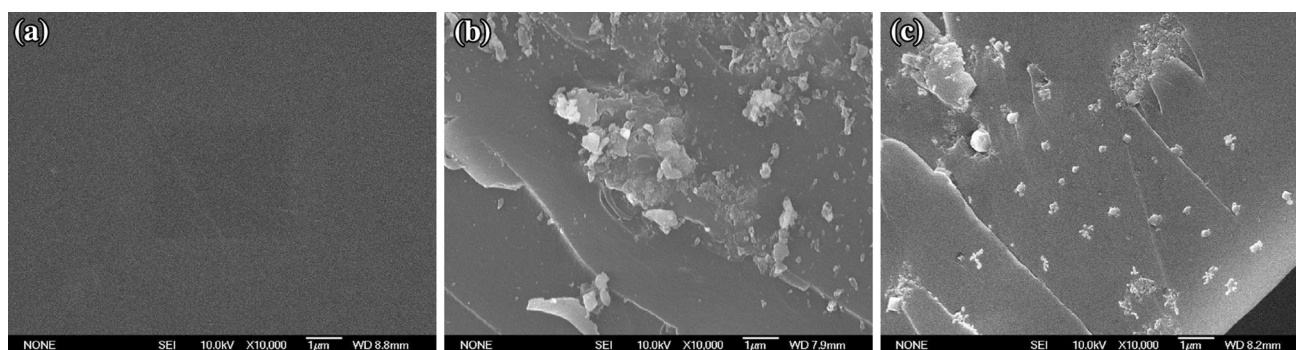


Fig. 8: The SEM images of (a) pure UV coatings, (b) UV coating with 2 wt% SW-silica, and (c) UV coating with 2 wt% PG-silica

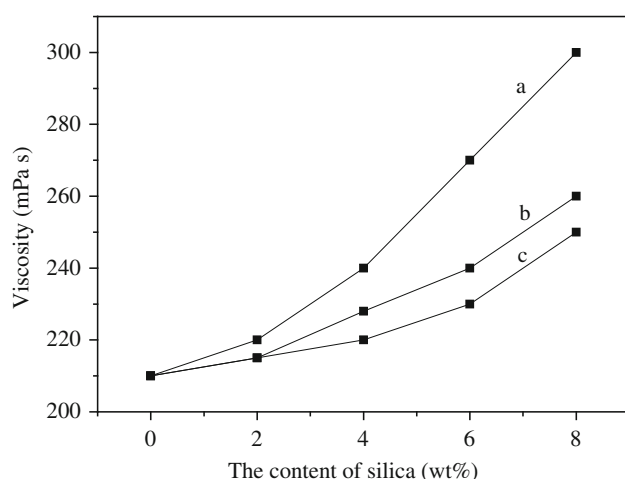


Fig. 9: The viscosity for coatings with various amounts of (a) nanosilica, (b) SW-silica, and (c) PG-silica

curable coatings vs their nanosilica and modified nanosilica contents are shown in Fig. 9. In comparison with the pure UV-curable coating, the coatings containing nanosilica or modified nanosilica had an increased viscosity. Moreover, the rate of increase, that is, the slope of the curve, is lower with the PG-silica than with the SW-silica. Both of them are significantly lower than with the unmodified nanosilica. One possible explanation is that nanosilica tended to self-aggregation in the UV-curable system and yielded highly viscous dispersions of UV-curable coatings due to their poor compatibility, and the enhanced interaction by higher nanosilica content resulted in the increasing viscosity.³⁶ After grafting with organic compounds, the organic shell will be formed on the nanosilica surface, and the nanosilica surface transfer from hydrophilation to organophilation, the stronger interaction between polymer matrix and nanosilica, decreases the viscosity of coatings. These results are in good agreement with the SEM analysis of UV cured films.

Table 1: The Shore D hardness for coatings with various amounts of nanosilica, SW-silica, and PG-silica

Content nanosilica (wt%)	Nanosilica	SW-silica	PG-silica
0	50	50	50
2	63	68	65
4	70	80	75
6	75	95	90
8	82	110	100

Effect of modified nanosilica on the hardness of UV-curable coatings

The hardness of the coatings, which is affected by the presence and dispersion of nanosilica particles, is the important factor affecting the abrasion and scratch resistance.³⁷ Table 1 summarizes the effects of nanosilica and modified nanosilica particles on the Shore D hardness of the UV cured films. The data show that the hardness increased with the increasing amount of modified nanosilica particles. The coatings with modified nanosilica exhibited higher hardness than those with unmodified nanosilica, which can be ascribed to the uneven dispersion of unmodified nanosilica in the polymer. The better dispersion increased the interaction of the nanosilica with the organic matrix, which improved the interface between the organic and inorganic phases and also increased the hardness. Surprisingly, the coatings with SW-silica show higher Shore D hardness than those with PG-silica at the same filling lever. At least three possible explanations can be reasonable for the phenomena. One is the grafting ratio, the higher grafting ratio, that is, the more organic materials on the nanosilica lead to a decrease in the films' hardness. The other is that the residual mercapto groups on the nanosilica surface of SW-silica can promote the UV curing process with higher crosslinking density by thiol-ene click reaction. The coatings with the higher crosslinking density always show a

higher hardness.³⁸ The last and the most important is the migration of nanosilica particles; the higher hardness can be attributed to the presence of the hard nanosilica particles, which probably can migrate partly toward the surface of the film.^{36,39} The lower grafting ratio of SW-silica particles leads to worse dispersion, which results in nanosilica that will migrate to the surface during the UV curing process rather than uniformly dispersing in UV cured films. However, as for unmodified nanosilica particles, two competing phenomena, namely migration and aggregation, would simultaneously occur. Aggregation of unmodified nanosilica would tend to prevent migration and would increase tendencies of nanosilica to remain in the bulk of the UV-curable coatings.⁴⁰

Conclusions

Surface modification and characterization of nanosilica with acrylsilane by “grafting to” method via two different grafting steps were investigated. The acrylsilane was prepared by thiol-ene click reaction between MPTMS and TMPTA, but it was prepared in advance via prepared-grafting method, while prepared on the nanosilica surface in step-wise propagation. The TGA results showed that the nanosilica prepared by the former method had a higher grafting ratio (143.2%) than that by the latter method of 21.9%. The result was further proved by the CA analysis of the compact nanosilica particles.

The modified nanosilica was used as an additive in the UV-curable coating, and the results showed that there are significant differences in their properties with the modified nanosilica from different grafting steps. The PG-silica showed better uniform dispersion in UV coatings than SW-silica. The viscosities of UV-curable coatings increased from 210 to 300 mPa·s, corresponding to the content of unmodified nanosilica increased from 0 to 8 wt%, while the value increased from 210 to 250 mPa·s for PG-silica and from 210 to 260 mPa·s for SW-silica. However, the hardness results showed the opposite trend; the hardness of coatings with PG-silica was lower than that with SW-silica. The results may be attributed to the multiple effects of the grafting ratio of polymer onto the nanosilica, the crosslinking density of UV cured films, and the dispersion of nanosilica particles in the organic matrix.

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