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Surface modification of nanosilica with 3-mercaptopropyl trimethoxysilane and investigation of its effect on the properties of UV curable coatings

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Abstract This paper describes surface modification of commercial nanosilica with 3-mercaptopropyl trimethoxysilane (MPTMS) and its effect on the properties of UV curable coatings. The mercapto groups were grafted onto nanosilica surface by a condensation of the surface Si–OH with the hydrolysized Si–OH of MPTMS. Fourier transform infrared spectroscopy, thermal gravimetric analysis, and particle size distribution were employed to characterize nanosilica and modified nanosilica. It was demonstrated that the mercapto groups were successfully grafted onto the nanosilica surface with the grafting ratio of 16.8% and the mercapto groups content of 0.9 mmol/g. The dispersion and self-aggregation of nanosilica in UV curable coatings were improved significantly. The photopolymerization kinetics of UV curable coatings, containing various amounts of nanosilica and modified nanosilica, were evaluated by the photo differential scanning calorimetry technique. This indicated that nanosilica both before and after modification decreased UV curing speed and ultimate percentage conversion; however, in comparison with the coatings containing unmodified nanosilica, the coatings containing modified nanosilica exhibited higher curing speeds and conversion ratios. It can be ascribed that the mercapto groups on the nanosilica surface reduced oxygen inhibition during the UV curing process via the thiol–ene click reaction. The mechanical properties of UV curable coatings were also compared.

Keywords Surface modification, Nanosilica, UV curing, Thiol–ene, Curing kinetics

Introduction

UV curable organic–inorganic nanocomposite coatings, which were usually prepared with nanosilica as an additive,[1–5] have attracted the attention of many researchers because of their remarkable mechanical properties and widespread potential applications.[6–9] The first issue concerned with the fabrication of these materials is how to disperse nanosilica particle components in UV curable coatings uniformly because of the extremely large surface-area/particle-size ratio of the nanosilica, and also how to avoid aggregation and phase separation. Many efforts have been made to obtain coatings with highly filled nanosilica particles and to yield a better dispersion or compatibility between nanosilica particles and host UV curable coatings. A common method is the surface treatment of nanosilica with a silane coupling agent, and vinyltrimethylsilane is recommended.[10] The second issue is how to reduce the negative effect of nanoparticles on the UV curing process and cured films because of the nanosilica scattering and reflection of UV light. In order to increase the curing rate and improve the mechanical properties of cured film, we had prepared polymeric nanosilica hybrid materials with nanosilica as node, isophorone diisocyanate and polypropylene glycol as link, and acrylate as terminal group; and

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polymerizable silica hybrid nanoparticles with tertiary amine structure.[11,12] It was found that the viscosity of the coatings decreased in comparison to the coatings with unmodified nanosilica, and the hardness and abrasive resistance of cured films were also improved with various amounts of modified nanosilica.

The organic–inorganic hybrid coatings based on the thiol–ene systems[13–16] combine the advantages of hybrid coatings and thiol–ene reactions, which make the UV curable technique more convenient. Besides improving the mechanical properties of coatings, they carry many other attributes for UV curable materials, including low oxygen inhibition, inherently rapid reaction rates, low polymerization shrinkage, free-photo-initiator polymerization, and the formation of homogeneous polymer structures.[13] However, in the case of the nanoparticles modified by silane and small thiol compounds always used as independent additives in the organic–inorganic thiol–ene system,[14–18] the awful smells of the small molecular thiol compounds and the self-aggregation of nanoparticles limit their applications. The problems can be overcome by grafting mercapto groups onto some polymers or nanoparticles. The nanoparticles modified by thiol silane are mostly used in removing of heavy metal, while their applications in UV curable coatings are few.[19] So the kinetics of UV curable coatings containing both nanosilica and mercapto groups deserve to be studied.

In this study, 3-mercaptopropyl trimethoxysilane (MPTMS) was applied as a nanosilica surface modifier for grafting mercapto groups onto silica nanoparticles, thereby improving the oxygen inhabitation during the UV curing process. Besides the grafting efficiency, particle size distribution, and dispersion of the nanosilica, its influences on the mechanical and physical properties of UV curing coatings were also investigated. In addition, photo differential scanning calorimetry (photo-DSC) was used as a tool to evaluate photopolymerization kinetics.

Experimental

Materials

Nanosilica powder (SP1) with an average particle size of 20–50 nm, a specific surface area of 640 m^2/g, and silanol group content of 1.9 mmol/g was obtained from Zhejiang Hongcheng Materials Co., China. MPTMS was purchased from Sigma Chemical Co. and was used as a coupling agent. Epoxy acrylate (EA) with double functionality, tripropylene glycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA) were provided by UCB Chemicals. 1-hydroxy-cyclohexyl-phenyl ketone (HCPK) from Ciba-Geigy was used as a free radical photoinitiator. All other chemicals were analytical pure reagents (AR) and used as received without further treatment.

Surface modification of nanosilica with MPTMS

Based on the previous references about surface modification of nanoparticles with MPTMS,[19,20] the modification process was carried out as follows: 10 g of nanosilica were kept in a vacuum chamber for 24 h at 100°C, and then dispersed in 150 mL anhydrous toluene by mechanical stirring (mechanical stirrer, IKA-P1, Germany) and ultrasonic dispersing (ultrasonic instrument, Bilon92-IID, China) for 30 min. The mixture was stirred at 300 rpm for a further 1 h, and then added into another prepared mixture consisting of 10 mL water, 10 mL anhydrous ethanol, 2 mL formic acid (as pH adjuster), and 75 mL of MPTMS by vigorous stirring. After continuously stirring for 4 h at reflux temperature, the obtained suspension was separated by centrifugation. After drying at 90°C under vacuum, the mixture was extracted using Soxhlet extractor for 12 h using toluene. Finally, the modified nanosilica was dried at 90°C under vacuum conditions for 12 h.

Preparation of UV curable coatings

The UV curable coatings used in this study were a mixture of 30 wt% EA, 40 wt% TPGDA, 25 wt% TMPTA, and 5 wt% HCPK. Various amounts (2.5, 5, 7.5, and 10 wt%, respectively) of nanosilica and modified nanosilica were directly added into the above mixure and dispersed by ultrasonic irradiation for 1 h at room temperature. Finally, the different hybrid coatings were obtained.

Characterizations

In order to estimate the subsistent degree of surface silanol groups, the –SH group on the nanosilica surface was determined by the reaction between the thiol compound and 5,5′-dithio bis-2-nitrobenzoic acid (DTNB) according to the method of Ellman: the DTNB transfer into thio bis-2-nitrobenzoic acid (TNB), which can be quantitatively detected by UV–Vis spectrophotometer.[21] Fourier transform infrared spectroscopy (FTIR) analysis was performed by mixing particles with dried KBr on a Nicolet 360 FTIR spectrometer collecting 16 scans in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. The thermo gravimetric analysis (TGA) was performed in a HCT-1 thermal gravimetric analyzer (Beijing Henven Scientific Instrument Factory, China) under a nitrogen atmosphere from room temperature to 700°C with heating rate of 20°C/min and flow speed of 50 mL/min. The grafting ratio (R_g) was calculated according to the following equation[22]:

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

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 particle (or particle agglomeration) size and distribution of nanosilica before and after modification were characterized by a laser particle analyzer Bettersize 2000 (Dandong Bettersize Instruments Corporation, Dandong, China). TPGDA was used as the following liquid.

The morphology of nanosilica and modified nanosilica were visualized by JEOL JSM-6700F field-emission scanning electron microscopy (FE-SEM). The powder was dispersed in acetone to prepare 1 wt% solution, and the solution was dropped onto the surface of a support, dried, and deposited on the sample with gold for SEM analysis.

The viscosities of the coating were measured by a NDJ-79 rotation viscometer (Shanghai Scientific Instrument Co., China) at 25°C. The Shore D hardness was determined according to the testing method of ASTM D2240. The UV curable system was processed by exposure to a medium pressure Hg lamp (1 kW, 80 W/cm^2) for 2 min and putting it in a dark place for 5 h.

The photopolymerization kinetics of UV curable coatings were studied by the photo-DSC (Q-1000 TA Instruments). The initiation light source was a 200 W medium pressure mercury lamp, which gave a UV light intensity at the sample of 50 mW/cm^2 over a wavelength range of 200–440 nm. Samples weighing 20 ± 0.1 (mean ± SD) mg were placed in uncovered aluminum pans, and a reference aluminum pan was left empty. The conversion of acrylate double bonds in the UV curable system was calculated by integrating the area of the exothermic peak.

Results and discussion

Preparation and characterization of modified nanosilica

The functional groups of nanosilica before and after modification were characterized by FTIR as shown in Fig. 1. In the spectra of MPTMS (curve a), the peak at 2570 cm^{-1} corresponds to –SH of MPTMS,[19] and the vibration bands at 2926 and 2855 cm^{-1} relate to the symmetric and asymmetric stretching of –CH$_2$,[11] which are also observed in the vibration spectra of modified nanosilica. From the FTIR spectra of nanosilica (curve b), we can see that the stretching vibration peaks of Si–OH reach near 3430 cm^{-1}, and the asymmetric stretching vibration is around 810 cm^{-1}, while the symmetric stretching vibration and bending vibration is near 470 cm^{-1} of Si–O–Si.[23] As the strength of peak at 3430 and 1650 cm^{-1} corresponding to –OH on the nanosilica surface decreases and the peak at 1100 cm^{-1} corresponding to Si–O–Si increases, it can be ascertained that the functional group –SH of MPTMS is successfully grafted onto the nanosilica surface. However, the appearance of the peak at 3430 cm^{-1} shows that –OH on the nanosilica surface has not reacted with MPTMS completely. The –SH and other peaks corresponding to MPTMS molecules could not be clearly observed in the spectra of modified nanosilica because of the strong vibration of nanosilica, which overlaps vibrations of MPTMS functional groups.

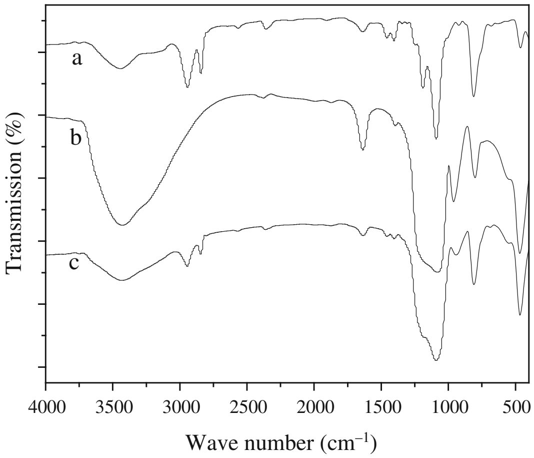

Fig. 1: FTIR spectra of (a) MPTMS, (b) nanosilica, and (c) modified nanosilica

It is difficult to quantitatively analyze the –SH concentration of modified nanosilica in FTIR spectra, and the method of Ellman is used to determine the –SH concentration of 0. 9 mmol/g. The detail process was as follows: the standard curve between the thiol group and UV absorbance of TNB was obtained by the reaction between thiol groups of MPTMS and DTNB. Then the thiol group of modified nanosilica was determined by UV–Vis spectrophotometer (Shimadzu, UV-3100PC).

On the basis of the above analysis, the idealized grafted mode for modified nanosilica is shown in Fig. 2.

The quantitative analysis of modified nanosilica and the grafting ratio were determined by TGA, which was performed from room temperature to 700°C by heating at 20°C/min. The result (Fig. 3) 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. The physically absorbed water was attributed to the weight loss up to 120°C, while the chemically bound water was attributed to the weight loss from 120 to 700°C.[24] As for modified nanosilica, there are two weight loss stages. The first weight loss occurred before 250°C, which can be ascribed to the physically absorbed organic compounds. The sharp weight loss from 250 to 700°C for modified nanosilica is probably attributable to large-scale thermal decomposition of MPTMS chains.[25–27] The obtained modified

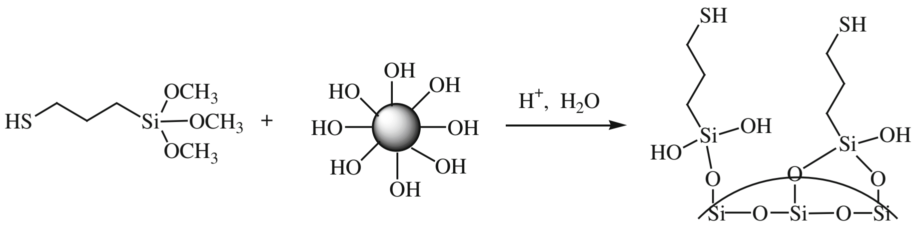

Fig. 2: The scheme for preparation of modified nanosilica

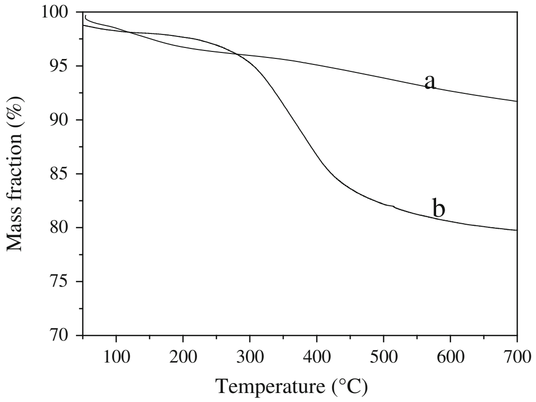

Fig. 3: The TGA thermogram curves of (a) nanosilica and (b) modified nanosilica

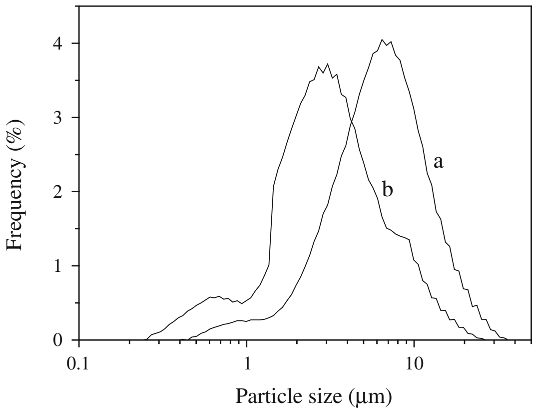

Fig. 4: Particle size distribution of (a) nanosilica and (b) modified nanosilica in TPGDA

nanosilica was dried at 90°C under vacuum conditions for 12 h and then extracted for 12 h, so it could be thought that the decomposition ratio of organic compounds was equal to the grafting ratio. The grafting ratio for modified nanosilica was 16.8%.

It is well established that the dispersion state of nanoparticles is a crucial factor in determining the final properties of nanocomposites. This is especially serious when the fabrication of composites with high amounts of nanoparticle content is attempted. It is essential to insure a good surface modification by MPTMS in obtaining monodispersal by sonication. The particle dispersion of nanosilica and modified nanosilica after 15 min sonication treatment is shown in Fig. 4. The average particle size of modified nanosilica is about 3 μm in TPGDA, which is larger than the real size of nanosilica because of the self-aggregation, but is smaller than the unmodified nanosilica dispersed by sonication in TPGDA (about 6 μm). It can be asserted that MPTMS has grafted onto the nanosilica surface.[22] The dispersion of nanosilica in organic solvent, more exactly, in TPGDA, was improved and the self-aggregation of nanosilica in UV curable coatings was reduced. The dispersion state of modified nanosilica and nanosilica in organic agents was further characterized by SEM, as shown in Fig. 5.

The morphology analysis of nanosilica and modified nanosilica by SEM shows the effect of MPTMS on reducing nanosilica's aggregation. Figure 5a shows that nanosilica existed in irregular blocks and aggregated extremely because of the large amounts of silanol groups on their surface. After being grafted with MPTMS, the silica existed in the state of irregular balls with a diameter of about 100 nm (Fig. 5b).

Effect of modified nanosilica on the curing kinetics

The formulations of the UV curable coatings used in this study were a mixture of 30 wt% EA, 40 wt% TPGDA, 25 wt% TMPTA, and 5 wt% HCPK. In this study, we varied the concentration of nanoparticles (including nanosilica and modified nanosilica) from 0 to 10 wt% based on the UV curable coating so as to investigate the effect of nanosilica and the surface functional group –SH on the curing kinetics of UV curable coatings.

The photopolymerization kinetics were identified by photo-DSC. The measured reaction heat during the photopolymerization was directly proportional to the number of vinyl groups in the UV curing system. And the integrated area under the exothermic peak was proportional to the percentage conversion of vinyl groups according to the following equation[28–30]:

$$\alpha = \Delta H_t / \Delta H_0^{\mathrm{theor}}$$

where ΔH_t is the reaction heat enthalpy released at time t and $\Delta H_0^{\mathrm{theor}}$ is the theoretical heat enthalpy for the complete conversion. For the UV curable coatings

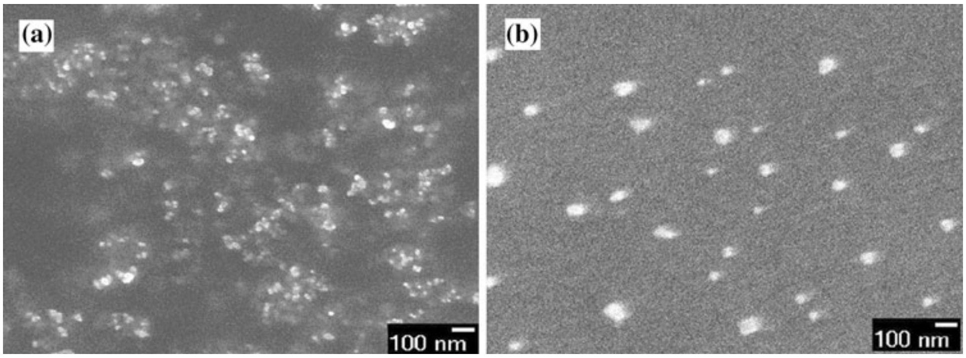

Fig. 5: SEM images of (a) nanosilica and (b) modified nanosilica

used in the study, $\Delta H_0^{\text{theor}}$ for EA, TPGDA, and TMPTA were 339, 542, and 818 J/g, respectively.[31] So the theoretical heat enthalpy for the mixture $\Delta H_0^{\text{theor}} = 550$ J/g according to their weight ratio of 30:40:25.

The kinetics parameters during the UV curing process were evaluated from the exotherm curves. The rate of polymerization (R_p) is related directly to the heat flow (*dH*/*dt*) using the following equation:

$$R_p = d\alpha/dt = (dH/dt)/\Delta H_0^{\text{theor}}$$

where *da*/*dt* is the conversion rate or the polymerization rate, and *dH*/*dt* is the measured heat flow.

Generally, the photo curing process is considered an autocatalytic curing reaction. The curing kinetics of an autocatalytic reaction are described by the following equation.[28–31]

$$d\alpha/dt = k\alpha^m(1-\alpha)^n$$

where *k* is the composite reaction rate constant, *m* is the order of the initiation reaction, and *n* is the order of the propagation reaction. Values of *k* and *n* can be determined from a ln–ln plot of $d\alpha/dt$ vs $\alpha^{m/n}(1-\alpha)$ derived from the equation:

$$\ln d\alpha/dt = \ln k + n \ln \alpha^{m/n}(1-\alpha).$$

The photo-DSC exotherms for the polymerization of the UV curable hybrid systems containing various concentrations of nanosilica and modified nanosilica are illustrated in Figs. 6 and 7. The results from the photo-DSC analysis are summarized in Table 1.

Figures 6 and 7 and Table 1 indicate that the exotherm and percentage conversion (which are related to the crosslink density) decreased as the concentration of nanosilica before and after modification in UV curable coatings increased from 0 to 10 wt%. This tendency may be attributed to the reflection and scattering effect of nanosilica on UV light; the nanosilica absorbed the incoming photons of UV light, thereby decreasing the photoinitiation efficiency. By comparing with nanosilica modification before and after, when the filling amount of silica nanoparticles was lower (2.5 and 5.0 wt%), the polymerization rate of UV curable coatings containing nanosilica were higher than the UV curable coatings with modified nanosilica, whereas the ultimate conversion was the opposite. This result is probably attributable to the higher amount of modified nanosilica, because the amount of modified nanosilica was calculated on the basis of bare nanosilica. The weight of silica nanoparticle powder was higher than nanosilica at the same filling level. The chance of self-aggregation increased and the radical mobility decreased. In contrast, this trend was reversed for silica nanoparticles at above 5 wt%. The UV coatings containing modified nanosilica exhibited higher exotherm and curing rates than the UV coatings with nanosilica. There are at least two factors that could be responsible for this behavior. One is the functional group of –SH on the surface of nanosilica, which reduces oxygen inhibition in the UV curing process by the thiol–ene click reaction as shown in Fig. 8. As the amount of modified nanosilica increases from 0% to 10%, the –SH content of the UV curable system rises from 0 to about 0.9 mmol/g × 10 g/(100 + 10 g) = 0.08 mmol/g = 16 mg/g. The active H atom of –SH on the surface of the nanosilica will transfer from peroxide radicals to thiol radicals, which can provide more active radicals for the UV curing process and initiate other acrylate structure, but cannot be terminated by other H atoms.[32] Another factor is that as the organic chain grafted onto the nanosilica increased, the dispersion of nanosilica in acrylate systems was improved and the self-aggregation decreased.

In addition, the values of the kinetics parameters *k* and *m* are consistent with the rules of exotherms and percentage conversions. While the amount of silica nanoparticles increased from 2.5 to 10 wt%, the reaction rate constant for UV curable coatings containing unmodified nanosilica decreased from 114.50 to 21.77 s^{-1}, and the value was from 114.50 to 33.65 s^{-1} for coatings with modified nanosilica. The initiation time increased from 51.0 to 60.0 s for coatings with unmodified nanosilica and to 57.0 s for coatings with modified nanosilica. It can be noted that the autocatalytic model

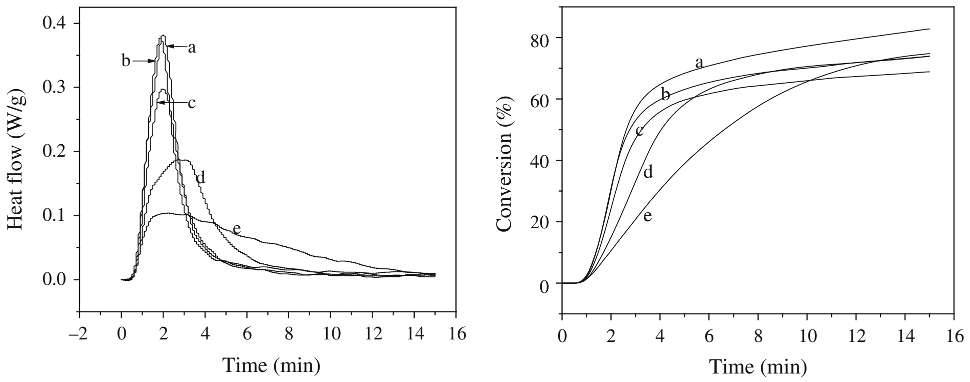

Fig. 6: Photo-DSC exotherms and percentage conversion for the UV curable hybrid coatings containing nanosilica: (a) 0%, (b) 2.5%, (c) 5.0%, (d) 7.5%, and (e) 10.0%

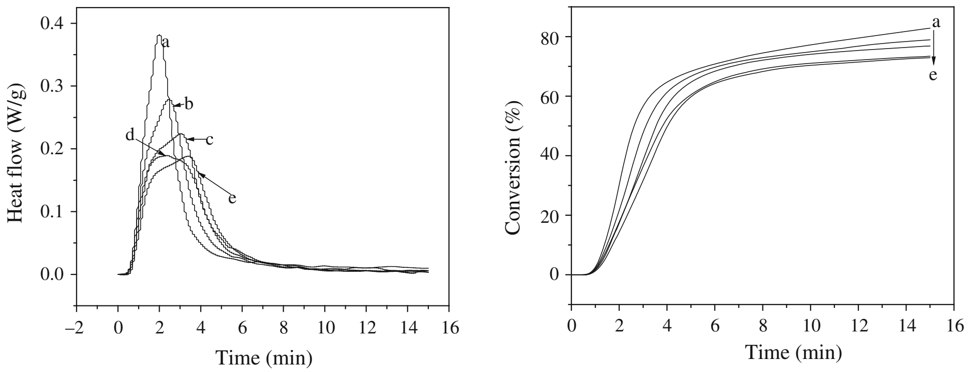

Fig. 7: Photo-DSC exotherms and percentage conversion for the UV curable hybrid coatings containing modified nanosilica: (a) 0%, (b) 2.5%, (c) 5.0%, (d) 7.5%, and (e) 10.0%

Table 1: Rate constants and reaction orders for the autocatalytic photopolymerization of silica-based compositions

The content of silica (%)[a]	ΔH (J/g)	Induction time (s)[b]	Peak maximum (min)	Conversion at peak (%)	Reaction order, m	Rate constant, k (s^{-1})
Nanosilica						
0	455	51.0	2.0	30.2	0.7879	114.50
2.5	406	53.4	1.9	27.2	0.6081	76.98
5.0	378	54.0	2.0	24.3	0.5241	52.58
7.5	406	57.0	3.1	35.0	0.5073	35.44
10.0	411	60.0	2.2	12.6	0.4793	21.77
Modified nanosilica						
0	455	51.0	2.0	30.2	0.7879	114.50
2.5	434	52.8	2.5	35.0	0.5806	55.16
5.0	423	54.0	3.1	40.8	0.5573	44.53
7.5	404	54.0	2.4	25.2	0.5251	38.33
10.0	401	57.0	3.4	39.1	0.4934	33.65

[a] The content of modified nanosilica was calculated as bare nanosilica according to the grafting ratio

[b] The time to attain a conversion of 1%

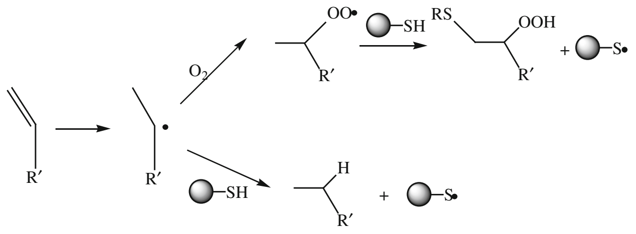

Fig. 8: Scheme for reducing the oxygen inhabitation effect of modified nanosilica

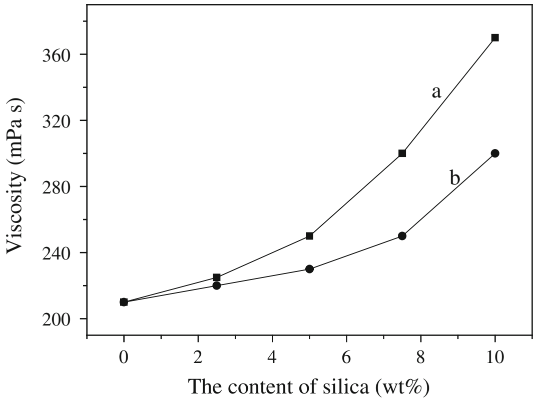

Fig. 9: The viscosity for coatings with various amounts of (a) nanosilica and (b) modified nanosilica

used to study the nanosilica effect on the photopolymerization is feasible because there is an induction period in the above curing process.

Effect of modified nanosilica on the properties 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 one of the most important parameters.[33] Thus, a suitable viscosity of the UV curable system is very important to the properties of the final cured film.[34] Figure 9 shows the viscosities of UV curable coatings with various amounts of nanosilica and modified nanosilica. It was found that the viscosity of the UV curable coatings increased as the filler (both modified nanosilica and unmodified nanosilica) concentrations increased, but the viscosity of UV curable coating with unmodified nanosilica was larger than that with modified nanosilica at the same filling level. It can be concluded that unmodified nanosilica tended to self-aggregation in UV curable systems and yielded highly viscous dispersions of UV curable coatings because of their poor compatibility with each other. After grafting with organic compounds, the organic shell is formed on the surface of the nanosilica, resulting in the transfer from hydrophilation to organophilation nanoparticles, which decreases the viscosity of the coatings. These results were in good agreement with the particle size distribution analysis.

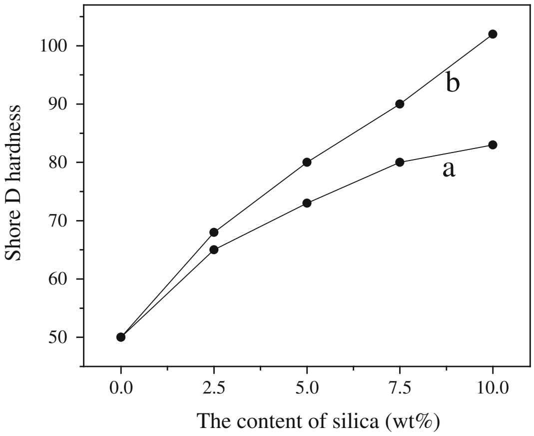

Fig. 10: The Shore D hardness for coatings with various amounts of (a) nanosilica and (b) modified nanosilica

The results of the Shore D hardness measurements are shown in Fig. 10. The value increases with the increase of the nanosilica weight ratio. This may be explained by the interaction of the nanosilica with the organic matrix, which improved the interface between the organic and inorganic phases and also could have increased the hardness. As for the higher addition amount, the difference between nanosilica modification before and after can be ascribed to the better distribution of modified nanosilica, therefore reducing the migration of inorganic nanoparticles during the UV curing process. The unmodified nanosilica is not homogeneously distributed and dispersed in the hybrid matrix, which may lead to phase separation and decreased hardness.[35] The other reason is the uniform distribution of nanosilica in the UV curable coatings and reinforcement by Si–O–Si linkage in the cured films.[6] The structure of the interpenetrating polymer network became much denser and the hardness of the material increased with the increased amount of silica.

Conclusions

Surface modification of nanosilica was prepared by grafting MPTMS onto the surface of the nanosilica. The results show that the –SH group was successfully grafted onto the surface of the nanosilica with a grafting ratio of 16.8% and –SH concentration of 0.9 mmol/g. The self-aggregation and the dispersion of nanosilica in UV curable coatings were significantly improved.

The kinetic parameters analysis indicated that UV curable coating containing at least 5 wt% modified nanosilica exhibited a higher curing rate and ultimate percentage conversion than that prior to modification. This can be ascribed to the functional group –SH on the surface of the nanosilica, which can reduce oxygen inhibition during the UV curing process by the thiol–ene click reaction.

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References

1. Sabzi, M, Mirabedini, SM, Zohuriaan-Mehr, J, Atai, M, "Surface Modification of TiO_2 Nano-particles with Silane Coupling Agent and Investigation of Its Effect on the Properties of Polyurethane Composite Coating." *Prog. Org. Coat.*, **65** 222–228 (2009)
2. Tomovska, R, Daniloska, V, Asua, JM, "Surface Modification of TiO_2 Nanoparticles via Photocatalytically Induced Reaction: Influence of Functionality of Silane Coupling Agent." *Appl. Surf. Sci.*, **264** 670–673 (2013)
3. Zhao, J, Milanova, M, Warmoeskerken, MMCG, Dutschk, V, "Surface Modification of TiO_2 Nanoparticles with Silane Coupling Agents." *Colloids Surf. A*, **413** 273–279 (2011)
4. Dastjerdi, R, Montazer, M, "A Review on the Application of Inorganic Nano-structured Materials in the Modification of Textiles: Focus on Anti-microbial Properties." *Colloids Surf. B*, **79** 5–18 (2010)
5. Karimi, L, Mirjalili, M, Yazdanshenas, ME, Nazari, A, "Effect of Nano TiO_2 on Self-Cleaning Property of Cross-Linking Cotton Fabric with Succinic Acid Under UV Irradiation." *Photochem. Photobiol.*, **86** 1030–1037 (2010)
6. Xu, JW, Pang, WM, Shi, WF, "Synthesis of UV-Curable Organic–Inorganic Hybrid Urethane Acrylates and Properties of Cured Films." *Thin Solid Films*, **514** 69–75 (2009)
7. Bauer, F, Flyunt, R, Czihal, K, Ernst, H, Naumov, S, Buchmeiser, MR, "UV Curing of Nanoparticle Reinforced Acrylates." *Nucl. Instrum. Methods B*, **265** 87–91 (2007)
8. Ranjbar, Z, Jannesari, A, Rastegar, S, Montazeri, Sh, "Study of the Influence of Nano-silica Particles on the Curing Reactions of Acrylic–Melamine Clear-Coats." *Prog. Org. Coat.*, **66** 372–376 (2009)
9. Sangermano, M, Malucelli, G, Amerio, E, Priola, A, Billi, E, Rizza, G, "Photopolymerization of Epoxy Coatings Containing Silica Nanoparticles." *Prog. Org. Coat.*, **54** 134–138 (2005)
10. Zhang, T, Wu, WJ, Mu, YP, "A Novel Nanosilica-Reinforced Waterborne UV-Curable Material." *Second International Conference on Smart Materials and Nanotechnology in Engineering*, Weihai, Oct 2009
11. Ma, GZ, Liu, W, Liu, XG, Wu, JB, Yan, T, Xu, BS, "Preparation and Properties of Polymerizable Silica Hybrid Nanoparticles with Tertiary Amine Structure." *Prog. Org. Coat.*, **71** 83–87 (2011)
12. Ma, GZ, Liu, W, Yan, T, Wei, LQ, Xu, BS, "Preparation of Polymeric Nanosilica Hybrid Materials and Their Properties." *Acta Polym. Sin.*, **2** 203–209 (2011)
13. Sangermano, M, Colucci, G, Fragale, M, Rizza, G, "Hybrid Organic–Inorganic Coatings Based on Thiol–Ene Systems." *React. Funct. Polym.*, **69** 719–723 (2009)
14. Clark, TS, Hoyle, CE, Nazarenko, S, "Kinetics Analysis and Physical Properties of Photocured Silicate-Based Thiol–Ene Nanocomposites: The Effects of Vinyl POSS Ene on the Polymerization Kinetics and Physical Properties of Thiol–Triallyl Ether Networks." *J. Coat. Technol. Res.*, **5** 345–351 (2008)
15. Colucci, G, Mana, S, Conzatti, L, Sangermano, M, "Hybrid Organic–Inorganic Silicate/Thiol–Ene Photocured Coatings." *Surf. Coat. Technol.*, **206** 2719–2724 (2012)
16. Korthals, B, Morant-Miñana, MC, Schmid, M, Mecking, S, "Functionalization of Polymer Nanoparticles by Thiol–Ene Addition." *Macromolecules*, **43** 8071–8078 (2010)
17. Chen, YZ, Wu, MH, Wang, KY, Chen, B, Yao, SZ, Zou, HF, Nie, LH, "Vinyl Functionalized Silica Hybrid Monolith-Based Trypsin Microreactor for On Line Digestion and Separation via Thiol–Ene 'Click' Strategy." *J. Chromatogr. A*, **1218** 7982–7988 (2011)
18. Lee, TY, Bowman, CN, "The Effect of Functionalized Nanoparticles on Thiol–Ene Polymerization Kinetics." *Polymer*, **47** 6057–6065 (2006)
19. Bach, LG, Islam, MdR, Kim, JT, Seo, SY, Lim, KT, "Encapsulation of Fe_3O_4 Magnetic Nanoparticles with Poly(methyl methacrylate) via Surface Functionalized Thiol–Lactam Initiated Radical Polymerization." *Appl. Surf. Sci.*, **258** 2959–2966 (2012)
20. Rao, AV, Bhagat, SD, Hirashima, H, Pajonk, GM, "Synthesis of Flexible Silica Aerogels Using Methyltrimethoxysilane (MTMS) Precursor." *J. Colloid Interf.*, **300** 279–285 (2006)
21. Shimada, K, Cheftel, JC, "Sulfhydryl Group/Disulfide Bond Interchange Reactions During Heat-Induced Gelation of Whey Protein Isolate." *J. Agric. Food Chem.*, **37** 161–168 (1989)
22. Guo, YK, Wang, MY, Zhang, HQ, Liu, GD, Zhang, LQ, Qu, XW, "The Surface Modification of Nanosilica, Preparation of Nanosilica/Acrylic Core–Shell Composite Latex, And Its Application in Toughening PVC Matrix." *J. Appl. Polym. Sci.*, **107** 2671–2680 (2008)
23. Chuayjuljit, S, Boonmahitthisud, A, "Natural Rubber Nanocomposites Using Polystyrene-Encapsulated Nanosilica Prepared by Differential Microemulsion Polymerization." *Appl. Surf. Sci.*, **256** 7211–7216 (2010)
24. Mueller, R, Kammler, HK, Wegner, K, Pratsinis, SE, "OH Surface Density of SiO_2 and TiO_2 by Thermogravimetric Analysis." *Langmuir*, **19** 160–165 (2003)
25. Qiu, FX, Zhou, YM, Liu, JZ, Zhang, XP, "Synthesis, Structural and Morphological Characteristics of P (MA-MPTMS)/SiO_2 Hybrid Nanocomposites." *Chem. J. Internet*, **6** 063020pe (2004)
26. Mikhailenko, S, Desplantier-Giscard, D, Danumah, C, Kaliaguine, S, "Solid Electrolyte Properties of Sulfonic Acid Functionalized Mesostructured Porous Silica." *Microporous Mesoporous Mater.*, **52** 29–37 (2002)
27. Kim, SS, Park, JE, Lee, J, "Properties and Antimicrobial Efficacy of Cellulose Fiber Coated with Silver Nanoparticles and 3-Mercaptopropyltrimethoxysilane (3-MPTMS)." *J. Appl. Polym. Sci.*, **119** 2261–2267 (2011)
28. Cho, JD, Hong, JW, "Photo-curing Kinetics for the UV-Initiated Cationic Polymerization of a Cycloaliphatic Diepoxide System Photosensitized by Thioxanthone." *Eur. Polym. J.*, **41** 367–374 (2005)
29. Cho, JD, Ju, HT, Hong, JW, "Photocuring Kinetics of UV-Initiated Free-Radical Photopolymerizations With and Without Silica Nanoparticles." *J. Appl. Polym. Sci.*, **43** 658–670 (2005)
30. Esen, DS, Karasu, F, Arsu, N, "The Investigation of Photoinitiated Polymerization of Multifunctional Acrylates

with TX-BT by Photo-DSC and RT-FTIR." *Prog. Org. Coat.*, **70** 102–107 (2011)

31. Palanisamy, A, Rao, BS, "Photo-DSC and Dynamic Mechanical Studies on UV Curable Compositions Containing Diacrylate of Ricinoleic and Amide Derived from Castor Oil." *Prog. Org. Coat.*, **60** 161–169 (2007)
32. Cramer, NB, Scott, JP, Bowman, CN, "Photopolymerizations of Thiol–Ene Polymers Without Photoinitiators." *Macromolecular*, **35** 5361–5365 (2002)
33. Yu, Y, Rong, MZ, Zhang, MQ, "Grafting of Hyperbranched Aromatic Polyamide onto Silica Nanoparticles." *Polymer*, **51** 492–499 (2010)
34. Qiu, FX, Xu, HP, Wang, YY, Xu, JC, Yang, DY, "Preparation, Characterization and Properties of UV-Curable Waterborne Polyurethane Acrylate/SiO_2 Coating." *J. Coat. Technol. Res.*, **9** 503–514 (2012)
35. Sangermano, M, Messori, M, "Scratch resistance Enhancement of Polymer Coatings." *Macromol. Mater. Eng.*, **295** 603–612 (2010)