

Preparation and Characterization of Scratch and Mar Resistant Waterborne Epoxy/Silica Nanocomposite Clearcoat

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ABSTRACT: Colloidal nano-silica particles were used to improve the scratch and mar resistance of waterborne epoxy coatings by directly blending. To enhance the compatibility of nano-silica particles within polymer matrix, nano-silica particles were first modified with 3-glycidoxypropyl-trimethoxysilane (GPTMS) and characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). The modified nano-silica particles were found to have a better dispersion and compatibility in the polymer matrix than the unmodified nano-silica particles.

Macro-scratch and nano-scratch testers were employed to characterize the scratch and mar resistances of the nanosilica-reinforced epoxy coatings. Relative to unmodified nano-silica, GPTMS-modified nano-silica particles can improve the scratch and mar resistance more significantly and reduce the transparency and gloss of waterborne epoxy coatings less seriously. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3634–3639, 2009

Key words: blending; epoxy coatings; silica; nanocomposites; scratch resistance

INTRODUCTION

Epoxy coating is one of the most widely used protective coatings because of its excellent chemical resistance, high strength, and strong adhesion to various kinds of substrates.¹ However, similar to other polymer coatings, its scratch and mar resistances needs further enhancement. Embedding with nano-sized inorganic particles has been proved as an efficient way.^{2–6} Among all the alternatives, nano-silica particles are most frequently used for the fabrication of transparent scratch and mar resistant coatings,^{7–10} because of its high hardness and relatively low refractive index. However, almost all the systems are involving the introduction of nano-silica into solvent-based epoxy coatings.^{11,12} With increasing environmental restriction, waterborne epoxy coatings are being developed quickly in the recent years¹³; therefore, how to improve the scratch and mar resistances of waterborne epoxy coatings is an urgent theme.

The mechanical properties of nanocomposite coatings are dependent on polymer matrix, the types of fillers, and the interactions between organic and inor-

ganic phases. A successful fabrication of nanocomposite coatings includes homogeneous dispersion of nanoparticles and strong interaction of nanoparticles with polymer matrix. Hydrophilic nano-silica particles can be well dispersed into the waterborne coating in its wet form, but aggregation might occur during drying because of the poor compatibility between hydrophilic nano-silica particles and hydrophobic polymer matrices. Dispersions of nano-silica particles in the formulating stage and in the drying stage seem to be two contradictive subjects for waterborne coatings. To overcome this problem, transformation of hydrophilic nano-silica particles into amphiphatic nano-silica particles would be an alternative method.

In this study, surface treatment of nano-silica particles in the water/ethanol media with 3-glycidoxypropyltrimethoxysilane (GPTMS) was carried out and then embedded into waterborne epoxy coating. The effects of nano-silica content and the amount of GPTMS used on the scratch and mar resistances, transparency, and gloss of the waterborne epoxy coating were investigated.

EXPERIMENTAL

Materials

Two-package epoxy clearcoats (one component is waterborne epoxy resin and the other is curing agent) and colloidal nano-silica sol (20 wt % in

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water, size = 10–20 nm, pH = 10) were supplied by Behr Processing Corp. (USA). GPTMS was purchased from Dow Corning Corp. (USA). Ethanol and acetic acid were obtained from Sinopharm Chemical Reagent Corp. (China). All the chemicals were used as received.

Preparation of Gptms-modified nano-silica particles

A certain amount of GPTMS was dissolved in ethanol (GPTMS:EtOH = 1 : 10) and followed by adding dropwise to the colloidal silica sol which had been acidified to a pH of 3–6 by acetic acid. The mixture was stirred at ambient temperature for 5 h to obtain a GPTMS-modified nanosilica sol. After reaction, the silica particles were purified by three centrifugation/redispersion cycles in water, and the solid content of the water dispersion used for the following experiments was 20 wt %.

Preparation of epoxy/silica nanocomposite coatings

A certain amount of GPTMS-modified nano-silica sol was added into the epoxy resin and mixed for 30 min at 1000 rpm using a high-speed shearing machine, and then cured by a curing agent based on the molar ratio of NH: epoxide of 1 : 1 under stirring for another 10 min. The obtained nanocomposite coatings were cast on Sn-coated ferrous plates and cured for 7 days at ambient temperature. The silica content was varied from 1 wt % to 4 wt % based on the total weight of the dried coatings.

Characterization

FTIR analysis was performed on a Magna-IRTM 550 spectrometer (Nicolet Instruments, Madison, WI). The scan wavelength was in the range of 400–4000 cm^{-1} . Thermogravimetric analysis was carried out with a Perkin-Elmer thermogravimetric apparatus (TGA-7, USA) under air and a heating rate of 10°C/min. DMA measurements were carried out on a DMA 242 (NETZSCH Inc., Germany). The tests were performed in the temperature range from 30 to 100°C at a heating rate of 5°C/min and with an oscillating frequency of 1 Hz. The morphologies of the nano-silica particles were observed by a transmission electron microscope Hitachi H-600, Hitachi Corp., Japan). The nanosilica particles dispersions in water were diluted and ultrasonicated at 25°C for 10 min and then dried onto carbon-coated copper grids before examination. Dispersion of nano-silica particles within the epoxy matrix was examined by a Philips XL30 model scanning electron microscope (SEM).

Scratch resistance of the coatings was measured by two different instruments: one is Multi-Finger Scratch/Mar Tester (Model 710, Taber Industries, USA) and the other is Automatic Scratch Tester (Sheen Instrument Ltd, UK). The former tester features five scratch tips with tip diameter that ranges from 1 to 7 mm. The tips with different loads (1.5 N, 3 N, 4.5 N, 6 N, 7 N) were applied to the panel beneath to produce an array of scratches. The lowest load which caused a complete and remaining mark was noted as the critical load (named as SR1). The latter tester is composed of a needle with a 1-mm tungsten carbide ball at its tip and a series of poise with mass from 100 g to 2 kg. The critical load (named as SR2) for scratching mark was justified with naked eyes. The transparency of the film was measured by a UV-1800PC spectrophotometer (Shanghai Mei-Pu-Da Instrument Corp., China). The scan wavelength was from 200 to 800 nm. The gloss (20°) of the coatings was measured by a haze-gloss tester (BYK gardener, Germany).

Mar resistance of the coatings, which reveals the ability to resist micro-scratches, was conducted with a Nano Indenter XP system (MTS Systems Corp., USA) using a procedure reported elsewhere.¹⁴ A Berkovich diamond tip with a diameter of 2 μm was used in the marring test. An initial surface profile of the sample was detected by a prescan procedure with a very small load. After that, a force linearly increased from 0 to 200 mN was applied to the coating film, and the surface profile was recorded by a depth sensor. A postscan was performed to determine the deformation recovery and the residual depth of the scratch after the diamond tip was removed. Five parallel scratches were carried out for each sample and the average value of the residual depth (a parameter for evaluation of the mar resistance) was adopted.

RESULTS AND DISCUSSION

Modification of colloidal silica with Gptms

Figure 1 presents the FTIR spectra of original nano-silica particles, GPTMS-modified nanosilica particles, and GPTMS. A peak at 911 cm^{-1} due to epoxy group and other two peaks at 2934.3 cm^{-1} and 2869.3 cm^{-1} due to stretching vibration of C–H bond are observed in the modified nano-silica particles, indicating that GPTMS has grafted onto the surfaces of the nanosilica particles.

The typical TGA curves of original and GPTMS-modified nanosilica particles with 30 wt % of GPTMS based on the weight of nano-silica particles as an example are shown in Figure 2. The total weight loss of 9.8% for GPTMS-modified nano-silica was much higher than that of 3.4% for original

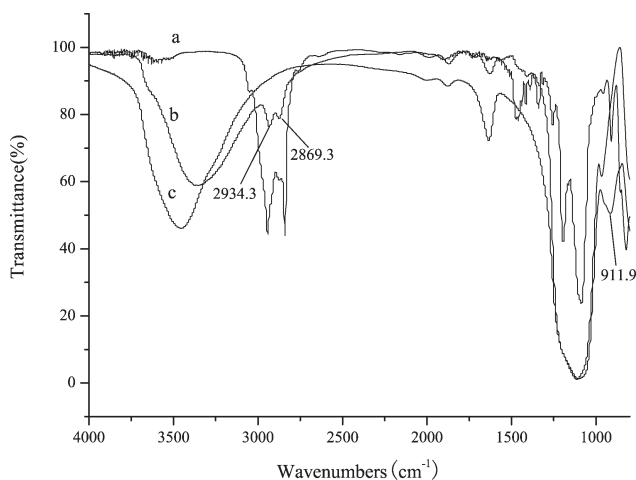


Figure 1 FTIR spectra of the GPTMS (a), GPTMS-modified nano-silica (b) and original nanosilica (c).

nano-silica, the increased portion could be ascribed to the grafted GPTMS. The amount of grafted GPTMS (m_{GPTMS} , mg) per gram of silica can be calculated from TGA data using Eq. (1):

$$m_{\text{GPTMS}} = \left[\left(m_{\text{GS}} - \frac{m_{\text{RGS}}}{P_{\text{UGS}}} \right) / \frac{m_{\text{RGS}}}{P_{\text{UGS}}} \right] \times 1000 \quad (1)$$

where m_{GS} is the mass of grafted silica sample before TGA measurement, m_{RGS} is the residue mass of the grafted silica sample after TGA measurement and P_{UGS} is the percentage residue mass of ungrafted silica. By using eq. (1), the amount of grafted GPTMS was calculated to be 71 mg/g of silica, indicating an efficient reaction between silica particles and GPTMS. Some further study on the structure of different silanes grafted onto silica particles were also reported by other researchers.^{15,16} The TEM image in Figure 3 displays that the GPTMS-modified nano-silica particles are homogeneously redispersed

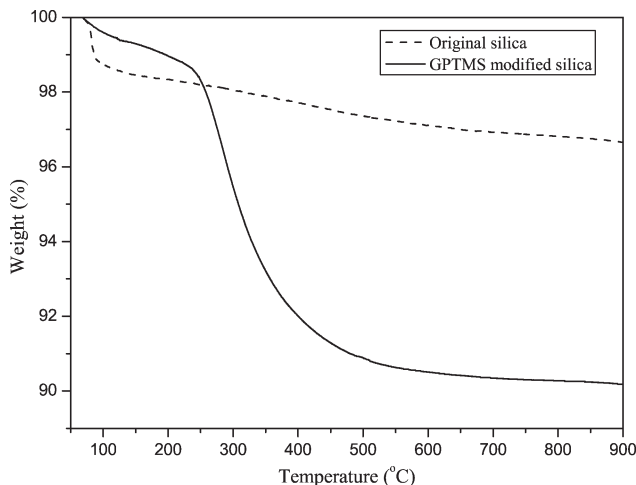


Figure 2 The TGA curves of original and GPTMS-modified nano-silica particles.

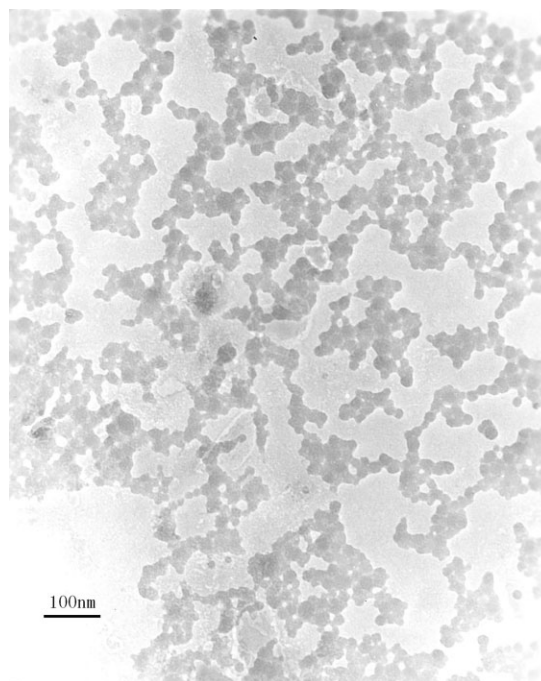


Figure 3 The TEM image of aqueous dispersion of GPTMS-modified nano-silica particles.

in water and have average diameter of about 15–20 nm.

Effect of nano-silica content on the properties of waterborne epoxy coating

Table I summarizes the scratch resistance and gloss of waterborne epoxy/silica nanocomposite coatings with different silica contents. When unmodified colloidal nanosilica was used, the scratch resistance in term of SR1 did not change until the silica content was up to 4 wt % while SR2 value increased as nano-silica increased. However, when GPTMS-modified nano-silica particles were embedded, both the SR1 and the SR2 values increased remarkably with increasing nano-silica content, indicating a better

TABLE I
Effect of Nanosilica Particles on the Film Properties

Nanosilica content wt %	SR1 N	SR2 (g)	Gloss (20°)	
Unmodified	0	3	400	74
	1	3	500	67
	2	3	500	60
	3	3	600	50
	4	4.5	800	49
Modified ^a	1	4.5	500	75
	2	6	800	72
	3	6	800	58
	4	6	900	53

^a 30 wt % of GPTMS (based on the weight of silica particle) was used in the modification of nano-silica particles.

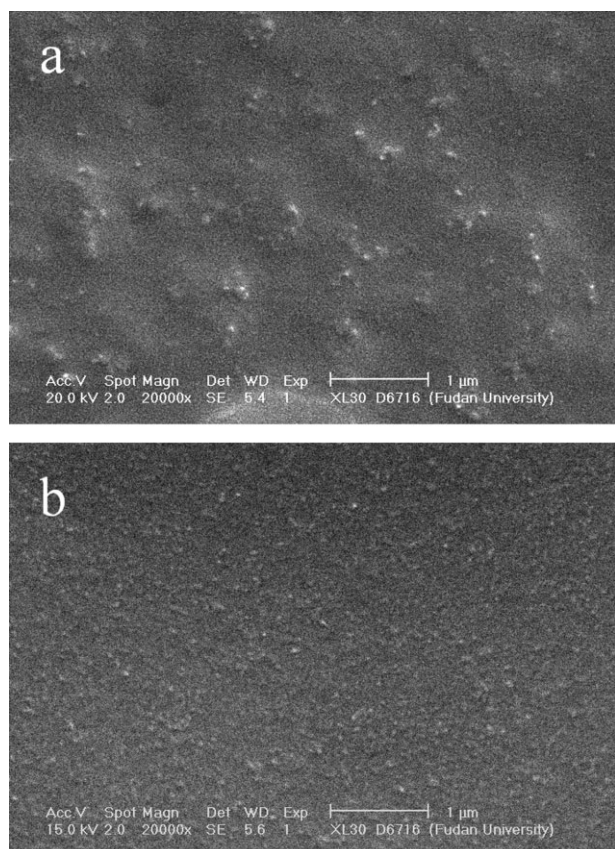


Figure 4 The SEM images of nanocomposite coatings containing (a) unmodified nano-silica and (b) GPTMS-modified nano-silica. (Nano-silica content = 2 wt %, Scale bar: 1 μ m).

improvement of the scratch resistance of waterborne epoxy coating by GPTMS-modified nano-silica. In addition, the gloss decreased seriously even after a very small amount of unmodified nano-silica was incorporated. Only 66% of the gloss of the pure epoxy remained at 4 wt % of nano-silica content. The reduction of gloss was caused by the increased diffuse reflection of visible light due to the silica aggregates-induced rougher surface. The series of coatings with GPTMS-modified nano-silica exhibited a slight reduction of gloss with increasing nano-silica content. At 2 wt % of silica content, the nanocomposite coating still kept 97% of gloss and possessed around two times of scratch resistance compared with the pure epoxy coating. Hence, 2 wt % of modified nano-silica would be ideal for the fabrication of scratch resistant and highly glossy epoxy coating. The reason why the modified nano-silica particles has better efficiency for the improvement of scratch resistance and less influence on the gloss of waterborne epoxy coating than the unmodified nano-silica particles, should be attributed to the higher compatibility and better dispersion of GPTMS-modified nano-silica in the dried coating. Figure 4 illustrates the SEM images of epoxy/silica nanocomposite

films. Aggregates are clearly seen on the film surface of the coating containing unmodified nano-silica [Fig. 4(a)] while the surface of the coating containing modified nano-silica [Fig. 4(b)] is rather smooth and no aggregates are observed. It appears that the composite coating embedded with the modified nano-silica particles contains a smaller filler domain and less agglomeration in the epoxy matrix. Accordingly, the surface modification with GPTMS on the nano-silica particles could improve the dispersion of silica. Moreover, as also considered by other researchers,¹⁷ the silica domains can be strongly interconnected with polymer network by GPTMS coupling agent and increase the crosslinking density, which cause an improvement on scratch resistance.

Figure 5 demonstrates the UV-vis spectra of epoxy/silica nanocomposite coatings. Only a slight reduction of the transparency of the nanocomposite coating was observed at more than 3 wt % of unmodified nano-silica and 4 wt % of modified

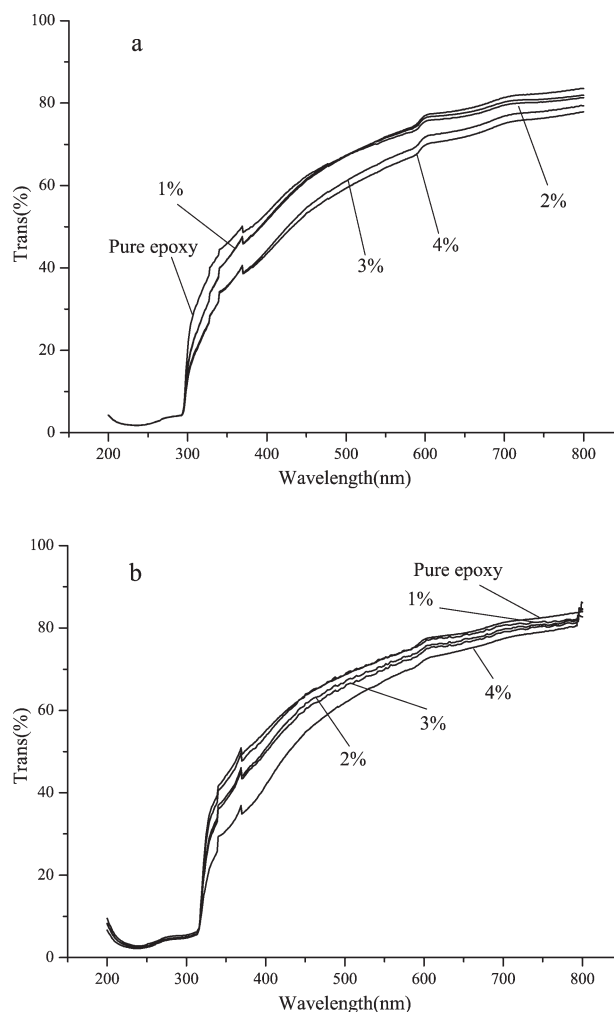


Figure 5 The UV-vis spectra of epoxy/silica nanocomposite coatings containing (a) unmodified nano-silica and (b) GPTMS-modified nano-silica.

TABLE II
Effect of GPTMS Content on the Scratch Resistance of Epoxy/Silica Nanocomposite Coatings (Silica Content = 2 wt %)

GPTMS content (wt %)	SR1 (N)	SR2 (g)
0	3	500
12	4.5	600
18	4.5	700
25	4.5	700
30	6	800
40	6	800

nano-silica, because of the strengthened reflection and refraction of light by silica particles and the interface between silica domain and polymer matrix. The other nanocomposite coatings nearly have the same transparency as pure epoxy coating. This is probably because of the low nano-silica content (1 ~ 4 wt %) studied.

Effect of the amount of Gptms on the scratch resistance of nanocomposite coating

To investigate the effect of GPTMS on the scratch resistance of epoxy/silica nanocomposite coatings, GPTMS concentration was varied from 12 wt % to 40 wt % based on the weight of nano-silica particles in the modification process. Table II gives the scratch resistance of their corresponding embedded coatings. Both SR1 and SR2 increase with increasing GPTMS concentration and tend to reach a plateau at the GPTMS concentration greater than 30 wt %. This might probably be attributed to the constant maximum grafting yield of GPTMS under the fixed reaction condition studied. Consequently, 30 wt % of GPTMS was adopted to modify the surface of nano-silica particles.

Mar resistance of waterborne epoxy/silica nanocomposite coatings

Nano-scratch test was performed to determine the mar resistance of the coatings. The penetration depth and residual depth profiles under progressive loading for pure epoxy coatings, and epoxy/silica nanocomposite coatings with either unmodified or modified silica are presented in Figure 6. Negative depth corresponds to the indent scratched by the tip and positive depth is due to the accumulation of debris in the scratch trace.

The pure epoxy sample shows an increase in penetration depth and residual depth as the load increased, and the residual depth is much shallower than penetration depth, which can be ascribed to the deformation recovery of the polymer. In the case of sample reinforced with original nanosilica, a slight

improvement of mar resistance is observed in terms of penetration and residual depth. But the recovery capability is reduced compared with pure epoxy, as its penetration depth is much shallower but the residual depth is almost the same with pure epoxy sample. This phenomena may be caused by two main factors: first, the particles within the polymer matrix leads to high stress concentration and hard film, so that the penetration depth can be decreased. Second, the introduction of inorganic particles leads to defects created at the interface because of a weak compatibility between the fillers and the matrix, which can increase the film brittleness. The two factors could make the film hard but brittle and they are responsible for the observed performance in penetration and residual depth. On the contrary, the sample reinforced with GPTMS-modified nanosilica reveals a profound improved penetration depth and residual depth. A better recovery capability after the load removal is also evidenced. These results are ascribed to the improved compatibility and strong chemical bonding between the particles and polymer matrix. The inorganic nanosilica domains embedded in polymer matrix, can restrict the motion of the polymeric segment and increase the crosslinking density of polymer network, which can improve its scratch and mar resistant properties. As a whole, the low penetration depth and high recovery (i.e., low residual depth) clearly demonstrate that GPTMS-modified nano-silica can improve the mar resistance of waterborne epoxy coating efficiently.

Dynamic mechanical analyses of the nanocomposite films

Dynamic mechanical analyses for the unmodified and modified silica-filled epoxy nanocomposites were conducted to examine the effect of the nanoparticles on the thermomechanical properties of the

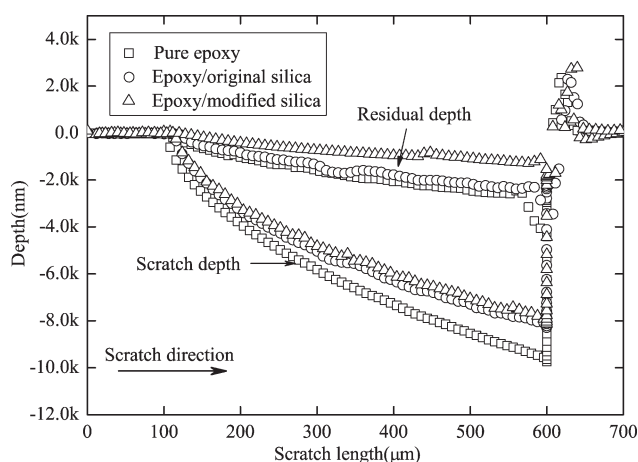


Figure 6 Profiles of penetration depth and residual depth of nano-scratch test.

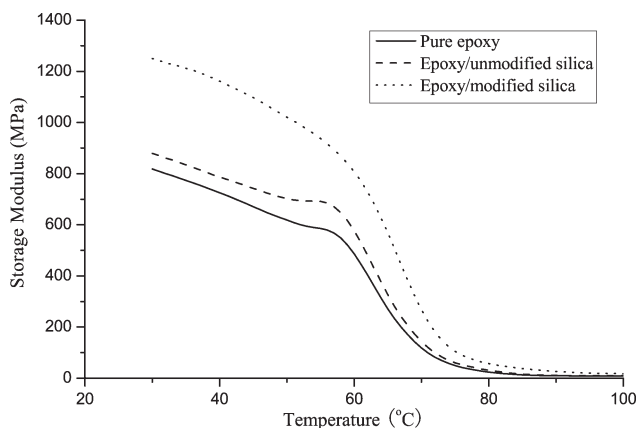


Figure 7 DMA curves of pure epoxy, epoxy/unmodified silica, and epoxy/modified silica.

epoxy coating films. Figure 7 shows the typical storage modulus (E') of the films as a function of temperatures from 30 to 100°C. Both the nanocomposite samples contained 2 wt % of silica, and the modified sample involved 30 wt % of GPTMS in the modification based on the weight of silica particles. It can be observed that the E' of the nanocomposite coatings is higher than that of pure epoxy throughout the temperature range studied. Additionally, the sample containing modified nanosilica presents a much higher E' than that with unmodified nanosilica, suggesting that the better dispersion of the nanosilica could reduce its domain size and make greater improvement on the modulus of the epoxy matrix. Moreover, the chemically bonded GPTMS on the silica surface could enhance the interfacial reaction between the inorganic silica phase and organic phase and increase the crosslinking density of the hybrid coating.

CONCLUSIONS

Epoxy/silica nanocomposite coatings were prepared by blending either unmodified or GPTMS-modified nano-silica particles with waterborne epoxy resin and curing agent. Both macro-scratch and nano-scratch measurements indicate that GPTMS-modified nano-silica particles can improve the scratch and mar resistance of epoxy coatings more efficiently than unmodified nano-silica. UV-vis spectra reveals

that the transparency of the epoxy coating is slightly influenced by the incorporation of unmodified or GPTMS-modified nano-silica in the range of silica content studied. The gloss of nanocomposite coating decreases with increasing silica content. However, the coatings containing GPTMS-modified nano-silica have much higher gloss than those containing unmodified nano-silica at the same load, because of the better dispersion of GPTMS-modified nano-silica particles in epoxy coating.

On the basis of this study, a waterborne transparent epoxy/silica nanocomposite coating with high scratch and mar resistance and high gloss can be prepared via addition of nano-silica particles. The hydrophilic nanoparticles also need surface modification to improve the mechanical properties of waterborne coatings, similar to how they work in solvent-based coatings.

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