Use of (Glycidoxypropyl)trimethoxysilane as a Binder in Colloidal Silica Coatings

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Received May 4, 1997. Revised Manuscript Received July 9, 1997[⊗]

Colloidal silica coatings were produced from suspensions of silica modified with (glycidoxypropyl)trimethoxysilane (GPS). Coating dispersions were prepared by adding GPS to a silica colloid (12 nm) suspension. Adsorption of hydrolyzed GPS species on silica surfaces was monitored by attenuated total reflection Fourier transform infrared spectroscopy. The addition of GPS to a basic silica suspension (pH 9.5) favored condensation among hydrolyzed GPS species over adsorption. By contrast, more adsorption on the silica colloids occurred in acidic suspensions (pH 4) and condensation among hydrolyzed GPS species was slower. The interaction between GPS and colloidal silica was also reflected in the aggregation and gelation behavior of the suspensions and the coating microstructure. Suspensions prepared by addition of GPS at low pH resulted in coatings that were less prone to cracking. In addition, polyamine could be added to these suspensions in order to cure the coatings. Compared with unmodified silica coatings, coatings prepared with GPS modification were denser, adhered better to the polymer substrate, and could be made thicker (up to 20 μm). Coatings were also transparent to the eye.

Introduction

Ceramic coatings with attractive thermal, chemical, electrical, and tailored optical properties can be prepared from suspensions of colloidal ceramics. Colloidal coatings represent one type of sol−gel coating in which the “sol” is a dispersion of colloidal ceramic particles and coatings “gel” as particles aggregate and pack during drying.[2,3] After drying, particles are held together by weak van der Waals bonds, and sintering is required to strengthen the coating and sometimes tailor the microstructure. Some potential applications of colloidal sol−gel coatings require deposition on paper and polymer substrates that cannot withstand the temperatures needed for sintering (typically >400 °C). For example, ceramic coatings are proposed for antistatic layers,[4] inkjet print media coatings,[5] and adhesion promoting subbing layers for photographic film.[6] Low-temperature processing is desired to minimize stress and cracking in multilayer coatings, as demonstrated by Floch and co-workers[7,8] in their research on colloidal sol−gel routes for laser-damage-resistant coating applications. While colloidal coatings have been prepared without sintering or additives,[9] these coatings are easily abraded.[7] Likewise, some very thin coatings can be bonded directly to polymer substrates by a primer layer and require no higher temperature treatment.[4] However, the usual method to enhance the strength of colloidal ceramic coatings is through the addition of organic additives or binders.

In ceramic processing, organic binders are typically used to provide strength at low temperatures and then removed by thermal treatment,[10] but for colloidal coatings prepared at low temperatures, the binder becomes an integral part of the final coating. Polymers such as poly(vinyl alcohol) and poly(vinylpyrrolidone) adsorb on ceramic particle surfaces and increase the strength of colloidal coatings.[5,8] The polymer content used in these coatings depends on the properties and microstructure desired in the final coating. At higher polymer contents, the coating microstructure contains a continuously connected polymer phase. Polymer latex particles are common binders for paper coatings and paint[11] which contain ceramic pigments and fillers. They have also been used as binders in colloidal indium oxide coatings.[12]

Organosilanes are an alternative to organic polymer binders. The structure of the silane $[\mathrm{Si(OR)}_x\mathrm{R'}_{4-x}]$ provides for bonding to the particle surface and chemical functionality that can be used to develop strong bonds between particles. The application of organosilanes in colloidal coatings has been reported by several researchers.[6,13−15] Van Ooij et al.[6] prepared coatings on

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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S0897-4756(97)00288-3 CCC: $14.00

polymer substrates using an aqueous silica colloidal suspension containing (aminopropyl)triethoxysilane. The coatings (90−200 nm thick) were designed as porous subbing layers for photographic film. Yajima et al.[13] propose organosilanes as binders for stannic oxide−zirconium oxide colloidal particles and design dense coatings for weathering resistance. These practical applications and our previous brief reports[14,15] indicate the potential for silanes as binders in colloidal coatings.

Application of organosilanes in colloidal sol−gel coatings requires attention to the reactions of the silane in the suspension medium and interactions with ceramic surfaces. Due to the wide use of organosilanes in applications such as primer layers and adhesion promoters in composites, there are numerous studies that address these issues.[16] For new coating systems, challenges remain in the understanding of the interactions between the silane and the colloidal particles so that the appropriate processing conditions and amounts of silane can be chosen, and coatings with the desired microstructure prepared. In this paper, we report on the use of (glycidoxypropyl)trimethoxysilane (GPS) as a binder in colloidal silica coatings with particular emphasis on the effects of suspension pH on silane adsorption and coating microstructure. GPS was chosen for this study as it has an epoxy group which can be used to form strong bonds between particles in a coating.

Experimental Section

Suspension and Coating Preparation. Suspensions for coating were prepared using a commercial aqueous silica suspension (Ludox LS, Aldrich Chemicals) with a silica particle size of 12 nm. Unless otherwise noted, the silica suspension was diluted from its original 30 wt % concentration to 10 wt %, using a solution of ethanol (50 wt %) and water (50 wt %). The pH of the silica suspension was adjusted by adding dilute HNO_3 or NH_4OH solutions while stirring. The pH was measured immediately after the addition of the acid or base. Two pH conditions were investigated: pH 4 and 9.5. (Glycidoxypropyl)trimethoxysilane (GPS, 98%, Dow Corning Chemicals) was used as-received. GPS was added dropwise to the silica suspension during vigorous stirring. The suspension prepared at pH 4 was stirred for 24 h, while the suspension prepared at pH 9.5 was stirred for only several hours. The GPS:silica weight ratio (R) was varied between 0 and 0.33. For the pH 9.5 suspensions with $R > 0.2$, NH_4OH solution was added to accelerate the hydrolysis of GPS and buffer the pH.

As an example of the procedure, the following steps were used to prepare a suspension with $R = 0.33$. Ludox LS (24.2 g of the 30 wt % as-received suspension), water (24.2 g), and ethanol (24.2 g) were combined in a 100 mL bottle. The pH was adjusted to 4 by the dropwise addition of 1 M HNO_3 solution. GPS (2.4 g) was then added to the suspension with vigorous stirring for 24 h.

Coatings were prepared by dropping the suspension on a poly(ethylene terephthalate) (PET, ICI-6138) substrate and spreading the coating suspension using a glass rod. The PET sheet was treated with amino groups to enhance hydrophilicity. Before deposition, triethylenetetramine (TETA, Aldrich Chemicals) was added to the GPS/silica suspension. The TETA was used to cure the epoxy groups. The amount of TETA was kept constant for all suspensions at a TETA:GPS molar ratio of 1:2. Coatings were prepared within 1−4 h after TETA was added. The coating thickness was controlled by the volume of the suspension and the area of the substrate. The wet coating was put in a drying oven with air convection at 80 °C for at least 2 h. Dry coating thicknesses were measured with a micrometer (±1 μm)

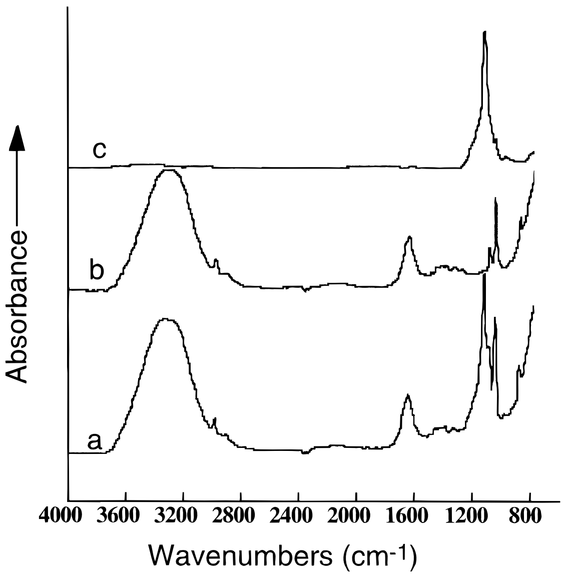

Figure 1. ATR-FTIR spectra of (a) a suspension containing colloidal silica, H_2O, EtOH, and HNO_3 in amounts used for coatings (see text); (b) a solution of H_2O, EtOH and HNO_3 of the same composition as that of the liquid medium in the suspension; and (c) a difference spectrum generated by subtracting (b) from (a).

Characterization. The coating suspensions were characterized by laser light scattering and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The particle or aggregate size in the suspension was determined by quasielastic laser light scattering (Coulter Model N4SD submicron particle analyzer). Suspensions were filtered (1 μm) before they were placed into the sample holders. The particle or aggregate size, which by this method is a hydrodynamic radius or diameter, was calculated by using unimodal analysis. ATR-FTIR (Nicolet Magna 750) was used for qualitative analysis of silanol content on particle surfaces for different reaction times and GPS:SiO_2 weight ratios (R). The data were gathered by spreading a sample of the suspension on the ZnSe ATR crystal and collecting spectra with an incidence angle of 45 °C. Analysis and comparison of ATR-FTIR data were made easier by subtracting a spectrum collected from a solution of H_2O, EtOH, and HNO_3 (the liquid medium used for suspensions) from the spectrum gathered for the silica suspension, as shown in Figure 1. Subtraction removes characteristic absorbances for ethanol and water. The prominent feature of the difference spectrum (labeled c) is an absorbance at $\sim$1120 cm^{-1} which corresponds to stretching of the SiO_4 tetrahedron.[17] ATR-FTIR analysis of suspensions containing colloidal silica and GPS focused on the region to the right of this absorbance (1050−700 cm^{-1}); the features of this region will be discussed later.

The microstructure of the coatings was characterized by optical microscopy (Olympics BX60), field emission scanning electron microscopy (SEM, Hitachi S-900) and nitrogen gas adsorption−desorption (Micromeritics ASAP 2000). The SEM samples were coated with platinum to eliminate charging effects, and a low voltage was used (3 kV). Nitrogen adsorption−desorption was used to determine the pore structure of

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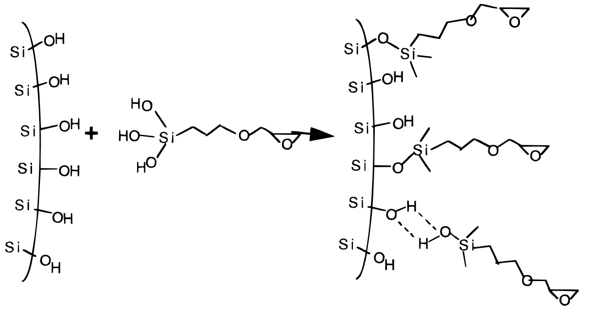

Figure 2. Illustration of GPS modification of colloidal silica showing condensation and hydrogen bonding between hydrolyzed GPS monomers and the silica surface, leaving the epoxy groups facing out. Other interactions between the GPS species and the silica are possible, including multilayer adsorption.

selected crack-free coating samples. The coatings were cut into small pieces (3 in. × 3 in.) and then were put into the sample holder and preheated at 100 °C for at least 2 h before testing.

Results and Discussion

GPS Solutions. The GPS monomer [$R'Si(OCH_3)_3$] contains three hydrolyzable alkoxy groups and an epoxy-functional organic chain. When GPS is added to water, it is initially immiscible; however, in the presence of a small amount of acid or base, the three methoxy groups hydrolyze [$R'Si(OH)_3$] and a single-phase solution results. The addition of alcohol to the solution enhances initial miscibility and therefore speeds hydrolysis. Hydrolyzed (and partially hydrolyzed) monomers then undergo condensation reactions to form dimers and larger oligomers. Pohl and Osterhaus[18] found that the hydrolysis rate was high in acidic or basic conditions with a minimum at pH 7 and that the condensation rate to dimers was lowest at pH 4. Thus, hydrolyzed monomers and low molecular weight oligomers are stable in the solution for hours or even days at pH ~ 4.[19] In higher pH solutions (>pH 8), the condensation reactions are faster and when the concentration of reactants is high enough, precipitates form and agglomerate and settle over time.

GPS–Colloidal Silica Suspensions. When GPS is added to an aqueous colloidal silica suspension, the hydrolysis and condensation reactions discussed above occur; in addition, hydrolyzed GPS monomers and oligomers can adsorb and react on the surface of the silica colloids. For surface modification (see Figure 2), the adsorption or condensation of hydrolyzed GPS monomers or small oligomers on the particle surface is desired. The pH conditions and suspension composition determine the extent of this surface modification as compared with condensation among GPS species. In our studies, the interaction between GPS species and colloidal silica particles was reflected by (i) the aggregation behavior and aggregate size in the GPS–colloidal silica suspension, (ii) the relative amount of surface silanols on the colloids, and (iii) the gelation behavior.

As-received, the Ludox LS suspension is stabilized by a base additive to pH 8–8.5. Direct addition of GPS to the Ludox suspension was difficult due to immiscibility.

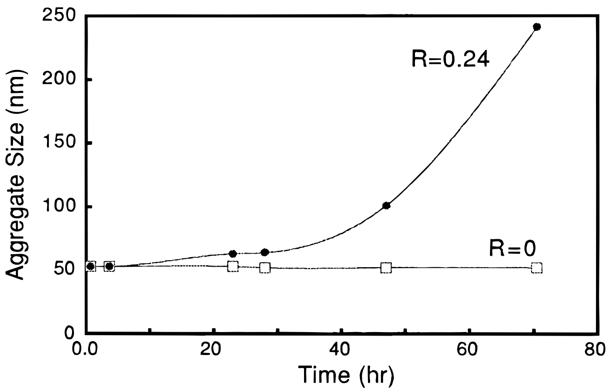

Figure 3. Effect of time on the silica aggregate size in suspensions (pH 4) with GPS ($R = 0.24$) and without GPS ($R = 0$). Aggregate size was measured by laser light scattering.

The immiscibility problem was overcome by adjusting pH (to 4 or 9.5) and adding ethanol to the suspension (to 33 wt % in the suspension). Like GPS solutions, basic conditions in the suspension promoted rapid condensation among silane monomers and oligomers. When the GPS-to-silica weight ratio (R) was 0.3 or higher, this rapid condensation resulted in the formation of precipitates which settled over time. After settling, the average particle size in the suspended phase was 15 nm, approximately the original size of the silica colloids. By contrast, addition of GPS to an acidified colloidal silica resulted in a uniform suspension. However, this suspension clouded over time, indicating aggregation.

Figure 3 compares the aggregation of a GPS–silica suspension with that of a silica suspension, both at pH 4. The 10 wt % Ludox-LS suspension had a constant aggregate size of 50 nm for at least 5 days. When GPS was added, the aggregate size increased slowly at first and then more rapidly after 24 h. Visually, the suspension became more and more cloudy with time. This size increase was also observed at lower GPS contents ($R = 0.07$). Upon addition to the acidic suspension, GPS monomers first hydrolyze and then start to adsorb onto silica particles (see FTIR results below) and also condense among themselves. Electrostatic stabilization of silica at pH 4 is relatively weak because the isoelectric point of silica is at pH 2.[19] While electrostatic repulsion appears to be sufficient to stabilize silica alone, it does not prevent aggregation in suspensions containing GPS. One possible explanation is that the adsorption of GPS on particle surfaces changes the distribution of surface charge and weakens repulsion. Additionally, because the modified surface is reactive (mainly due to additional silanols), particles are more likely to aggregate as they approach one another.

After 24 h, the aggregation could be reversed by adjusting the pH of the suspension to basic conditions (pH > 8). The suspension changed from cloudy back to nearly as clear as it was before GPS was added. The aggregate size was reduced to 45 nm and remained constant for at least 5 days. Aggregates in the silica suspension without GPS also reduced their size to 39 nm after pH adjustment. This GPS–silica suspension (prepared by GPS addition and aging at pH 4 and then pH adjustment to pH 9) was stable and did not gel. When an identical sequence was carried out on a GPS solution (without silica), the solution gelled. This

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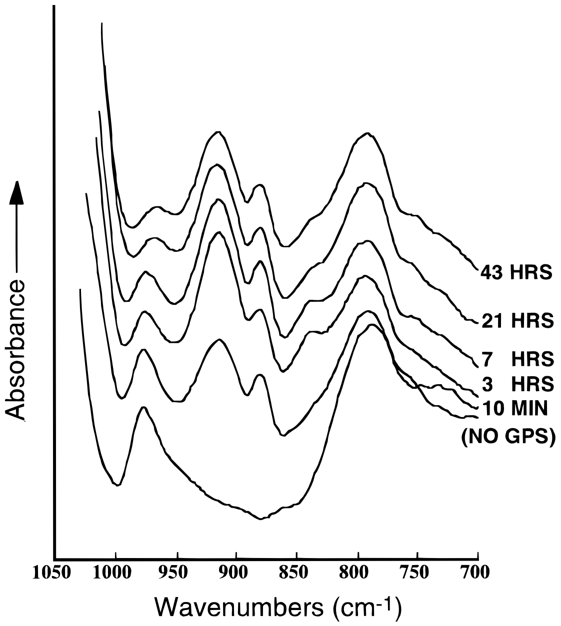

Figure 4. ATR-FTIR difference spectra for a colloidal silica suspension containing GPS ($R = 0.24$). Data are shown for increasing time after adding GPS to the suspension at pH 4.

comparison indicates that some or all of the GPS adsorbs on the silica surfaces at low pH and therefore cannot polymerize in the same way as free GPS when the pH is raised.

ATR-FTIR results support the conclusion that GPS adsorbs on silica particles under acidic conditions. Figure 4 shows the change in the ATR-FTIR difference spectra with time after GPS addition at pH 4. The data were gathered by spreading a sample of the suspension on the ATR crystal and then repeating with new samples after longer aging times. In the spectra, the absorption band around 970 cm^{-1} is assigned to the stretching of terminal Si$-$OH on the surface of silica particles.[17,20] The intensity of the 970 cm^{-1} band decreases when GPS is mixed into the suspension, reaching a constant intensity after 25 h. The data confirm the reaction of hydrolyzed GPS monomers or oligomers with surface silanols but do not provide information as to whether GPS condenses with the surface or is hydrogen bonded. Unfortunately, the surface silanol peak at ~3740 cm^{-1} could not be analyzed in these samples. The absorption at around 915 cm^{-1} is assigned to nonbridging Si$-$OH stretching from GPS species.[17] This peak first increases with time due to hydrolysis of the GPS monomer and then decreases, indicating condensation among GPS species. While we did not monitor the epoxy ring-opening reaction, the results of Xue et al.[21] indicate that greater than 90% of the epoxy rings will be retained after 24 h. ^{29}Si NMR results on identical suspensions show rapid and complete hydrolysis of GPS, followed by a disappearance in the monomer signal due to adsorption.[22]

The adsorption of GPS on the silica surface is also evidenced by comparing the changes of Si$-$OH band at 970 cm^{-1} for suspensions with different amounts of GPS (Figure 5). These data were taken after 24 h at pH 4. The suspension with the greatest amount of GPS addition had the lowest intensity for the Si$-$OH band at 970 cm^{-1}. As the GPS:SiO$_2$ ratio decreased, the intensity increased, indicating that more surface silanols remain. The data also show an increase in the intensity of the 915 cm^{-1} band for Si$-$OH on GPS as the relative amount of GPS in the suspension increases. While these data show important general trends, they do not provide quantitative information on the amount of adsorbed GPS and free GPS for a given GPS:silica ratio.

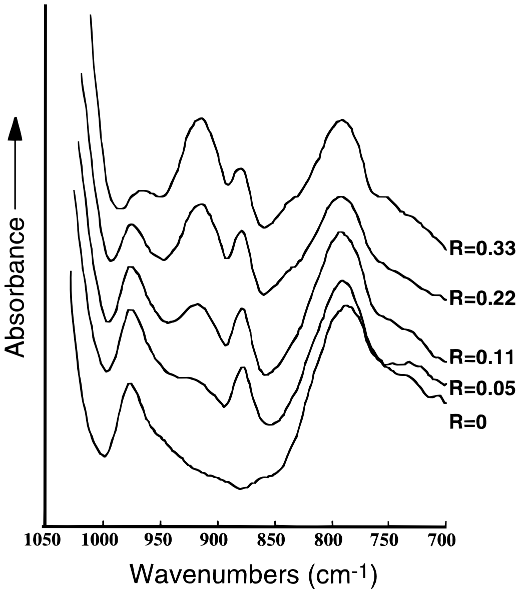

Figure 5. ATR-FTIR difference spectra for colloidal silica suspensions containing different relative amounts of GPS added to the suspension at pH 4. Data were taken 25 h after GPS was added to the silica suspension. R = GPS:SiO$_2$ by weight.

GPS-modified silica particles have epoxy functionality and can be cross-linked by an amine curing agent (triethylenetetramine, TETA). As discussed above, colloidal suspensions prepared with GPS addition at pH 4 followed by aging and pH adjustment to 8$-$9 were stable for several days. However, when the amine curing agent was added, the suspensions gelled (i.e., became semisolids which did not flow on tilting their containers). An investigation of the effect of GPS content ($R = 0-0.12$) on gel time of suspensions containing a constant relative amount of TETA (TETA:GPS molar ratio = 1:2) was carried out.[14] The R values chosen for this study were low, and hence the majority of the silane was likely adsorbed onto the colloid surfaces. The results showed that the gelation time decreased from ~300 h for the suspension with $R = 0.03$ to 5 h for the suspension with $R = 0.12$. Suspensions without TETA addition did not gel for all R values, indicating enhanced silanol condensation accompanying pH adjustment to 9 was not responsible for the gelation. Also, the addition of TETA to colloidal silica (without GPS modification) did not result in a uniform gel, but rather small clumps (millimeter size) of particles. Therefore, the gelation of GPS-modified silica suspensions is related to the curing of the epoxy-functionalized particles and silane species in solution. For the preparation of coatings, the reactivity of the amine and epoxy groups at room temperature indicates that the time available to form the coating

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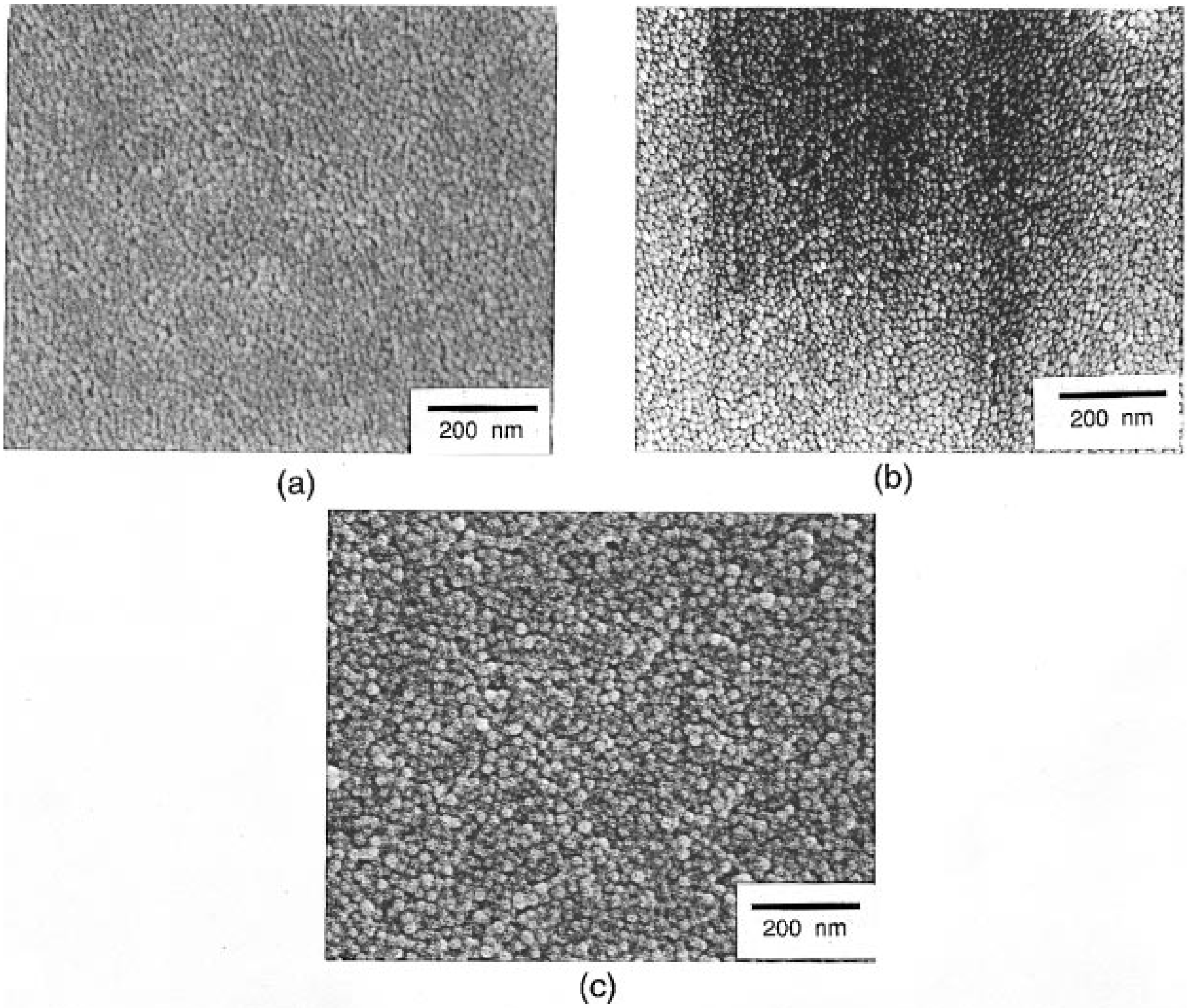

Figure 6. SEM photomicrographs of the surfaces of coatings prepared from (a) a colloidal silica suspension (Ludox LS diluted to 2 wt %), (b) a colloidal silica suspension with GPS ($R = 0.33$) added at pH 8, and (c) a colloidal silica suspension with GPS ($R = 0.33$) added at pH 4 with TETA added (molar ratio TETA:GPS = 1:2).

(shelf life) will be limited by the amount of GPS and amine present.

The 24 h stirring of the suspension at pH 4 was essential. Since the condensation rate is low at this pH, this aging time was needed for the hydrolyzed GPS to adsorb on particle surfaces. The above gelation experiments were repeated for suspensions prepared with only 30 min of stirring at pH 4 followed by pH adjustment to pH 8. These suspensions gelled without TETA addition. Since most of the GPS condensation occurred at high pH, the gel is dominated by siloxane bonding.

Coatings. The microstructures of unmodified and GPS modified colloidal coatings also reveal the interactions in suspensions. Figure 6 shows SEM micrographs of coating surfaces. The coating prepared from unmodified silica is composed of well-packed particles (~12 nm). With GPS addition at pH 9, the coatings have a similar microstructure with silica particles of about the same size. However, GPS modification under acidic conditions (with pH adjustment to pH 8 and TETA addition) leads to particles which are measurably larger in size (~20 nm). While aggregation was noted in these suspensions (see Figure 3), the larger particles are too small to be aggregates (which were measured to be 45 nm in size after pH adjustment). The particle size increase is indicative of multilayer adsorption of silane on the particle surfaces and is consistent with gelation and ATR-FTIR observations.

Silica coatings (without GPS modification) were prepared by depositing an aqueous colloidal silica suspension (Ludox LS diluted to 2 wt % SiO_2) onto a PET substrate. These coatings were porous with a surface area of 300 m^2/g, as determined by N_2 gas adsorption. The coating thickness was limited to about 1.5 μm. Thicker coatings were cracked and adhered poorly. Cracking is linked to capillary stresses that develop during drying.[23]

The microstructure, cracking behavior and mechanical performance of the coatings were influenced by GPS modification procedure, the GPS:SiO_2 ratio (R) and the addition of a curing agent. Optical photographs (Figure 7) show that if GPS was mixed directly into the Ludox suspension (pH 8) with R less than 0.3, the resulting coatings exhibited cracking behavior similar to unmodified silica coatings. The addition of TETA had no effect in this case. When R was higher than 0.3, the coating suspensions contained precipitates and also cracked with or without amine addition. Under basic conditions, the GPS reacts quickly and does not adsorb on particle

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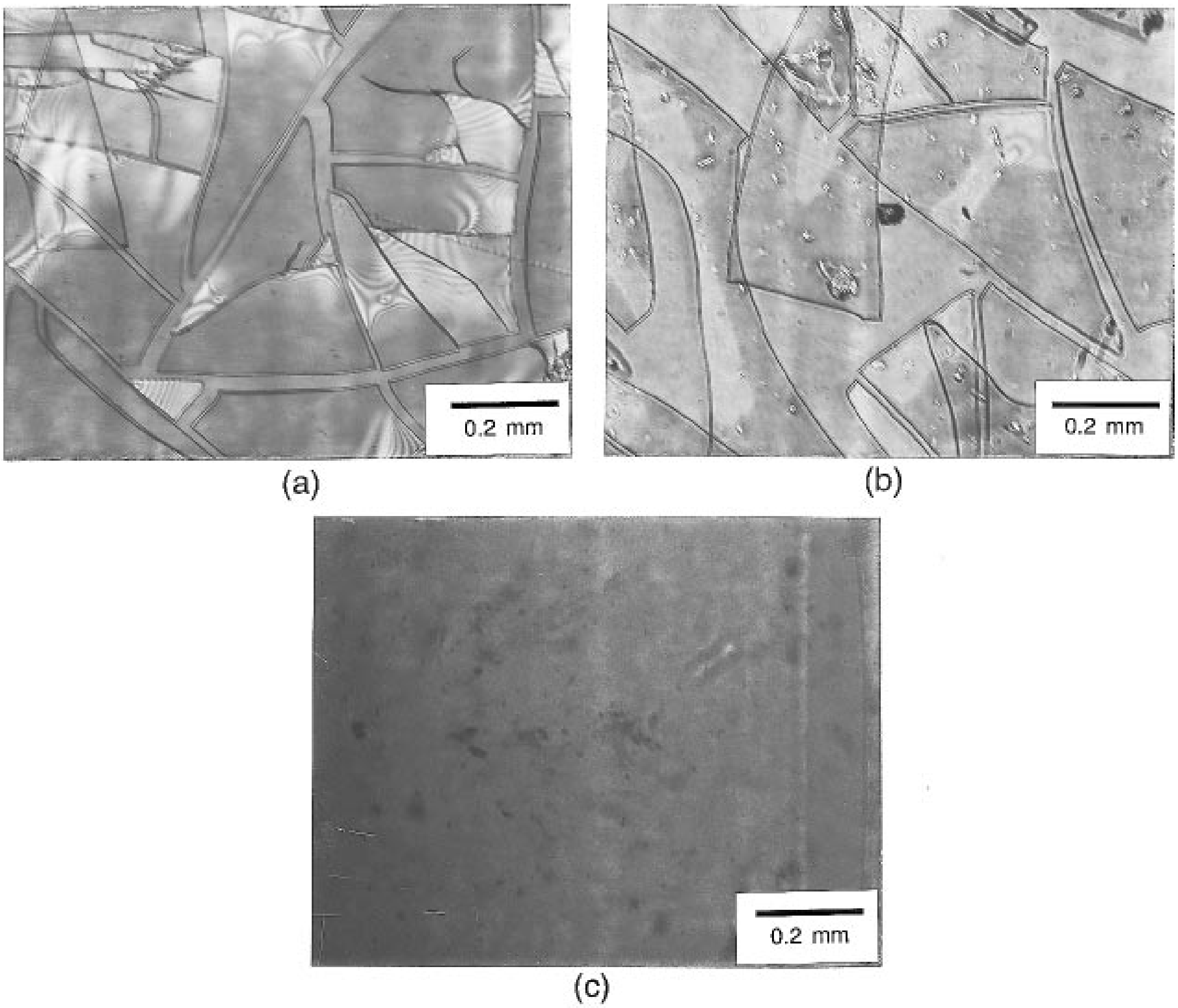

Figure 7. Optical photographs of coatings prepared from of the surfaces of coatings prepared from (a) a colloidal silica suspensions (Ludox LS diluted to 2 wt %), (b) a colloidal silica suspension with GPS ($R = 0.33$) added at pH 8, and (c) a colloidal silica suspension with GPS ($R = 0.33$) added at pH 4 (molar ratio TETA:GPS = 1:2).

surfaces. Therefore, the addition of the GPS did not help to bind the particles together and did not prevent cracking.

Coatings prepared by GPS modification under acidic conditions and polyamine addition gave the best results. As discussed above, these conditions led to adsorption of GPS on the particles and allowed the formation of amine-epoxy linkages. Thicker coatings could be prepared without cracks and the adhesion was improved. The maximum coating thickness increased with the GPS content. A final thickness of 20 μm was achieved for an R value of 0.33. These thick coatings were also transparent to the eye and showed type one nitrogen adsorption−desorption isotherms, indicating a nonporous structure. The lack of open porosity in these coatings suggests that excess siloxane fills the interstices between particles. Also, the lack of porosity eliminates the capillary drying stresses.

Acknowledgment. The authors thank J. Sefcik and Prof. A. V. McCormick for helpful discussions and interaction. Research support from the NSF Center for Interfacial Engineering and Rexam Graphics Company is gratefully acknowledged.

CM9702880