

# Self-Assembling Metal Coatings from Phosphated and Siloxane-Modified Polyurethane Dispersions: An Analysis of the Coating–Air Interface

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**ABSTRACT:** Polyurethane dispersion coatings containing phosphate and siloxane chains were evaluated for their self-assembling properties for a single-coating system. Dynamic contact angles (DCAs) and X-ray photoelectron spectroscopy (XPS) were used to study the coating–air interface. The siloxane chains were the predominant species on the surfaces of the coatings. The wetting properties of the coating–air interface were reversed when the coated panels were

immersed in an ionic solution, and the decrease in hydrophobicity was linear with time. Results from XPS and DCA analyses were similar. The self-assembling properties of the coatings could be useful in the development of hydrophobic coatings from hydrophilic polymers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 893–899, 2003

**Key words:** polyurethanes; self-assembly; X-ray

## INTRODUCTION

The behavior of macromolecules near the surfaces and interfaces of organic coatings often has a significant effect on the numerous properties of the coatings and plays a vital role in their applications. Therefore, an understanding of the interfaces responsible for durability, adhesion, and mechanical properties, on a molecular level, is important for the development of new generations of organic coatings. A common feature of all multiphase polymers is the presence of large interface areas. The properties of the interface are central to the properties of the coatings, and the ability to understand the interface is regarded as a key feature in developing and optimizing improved coating materials. The coating interface may be with air, another coating, or an inorganic surface, such as a metal. Interfaces involving polymers are generally of finite thickness. Therefore, the portions of a polymer adsorbed to a substrate or to a coating–air interface may differ from those in the bulk of the polymer. It is important to determine interface properties, but they are generally difficult to characterize, and reliable information is neither easily obtained nor readily available. The interface may form in a process that has not reached equilibrium, and the kinetics and thermodynamics must be taken into account.<sup>1</sup> For instance, the diffusion of species toward or away from the interface

may be slow, relative to the timescale of coating, and a nonequilibrium composition profile may be kinetically trapped as the temperature drops or as crosslinking increases.

In this article, we report on the coating–air interface of phosphate- and siloxane-containing polyurethane dispersions developed for a single-coating system for metal coatings.

## EXPERIMENTAL

Phosphate- and siloxane-containing polyurethane dispersions were prepared by a conventional method from hydroxyl-terminated phosphated and siloxane macroglycols, as described in an earlier article.<sup>2</sup> Different coating compositions were made by the mixing of the polyurethane dispersions with methylated melamine resin (used as a crosslinker) and thermal curing.

### Characterization

Determination of the dynamic contact angle (DCA)

A Wilhelmy-type wetting force was used to measure the advancing and receding contact angles. This method, which involves the measurement of the wetting force of a probe liquid up and down on the surface of any flat, solid sample, gives true advancing and receding contact angles. The more commonly used nonmoving sessile drop method does not adequately cover the polymer surface, and a small amount of evaporation of the drop can also rapidly change the contact angle.<sup>3</sup> In this study, a Cahn DCA-

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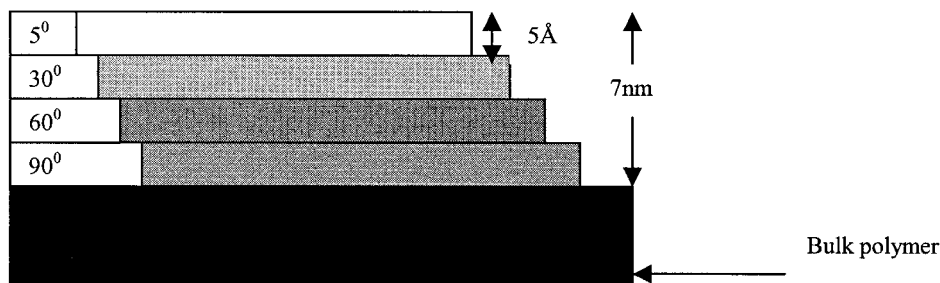


Figure 1 Schematic representation of the surface layers of the coatings analyzed by angle-dependent XPS.

322 analyzer (Cahn Instruments, Madison, WI) operating at 25°C and at a velocity of 100  $\mu\text{m/s}$  was used to evaluate the self-assembly nature of the phosphated and siloxane-modified polyurethane coatings by contact-angle measurements. Distilled water was used as a wetting medium. Hot-dipped galvanized steel panels were cut to 1.5 cm  $\times$  1.5 cm and dipped into a mixture of an aqueous polyurethane dispersion (ca. 10 wt %) and a melamine crosslinker. The coatings were then hooked with a spring and suspended in a curing oven. Curing was performed at a peak metal temperature of 230°C for 20 s. In some instances, curing was not done, and films were simply dried at 80°C for 30 min.

#### X-ray photoelectron spectroscopy (XPS) analyses

XPS is one of the most popular and useful methods for analyzing the surface compositions of coatings. XPS probes a coating layer to a depth of about 7 nm. Angle-resolved XPS is a technique by which a thin layer can be probed, with the sample tilted to change the angle of the surface with respect to the detector.<sup>4</sup> At small takeoff angles, the detector will only collect electrons emitted from the shallow region near the surface. At high takeoff angles, the detector will collect electrons emitted from both the shallow region and the deeper layers, as presented schematically in Figure 1. Therefore, with a change in the takeoff angle, a concentration depth profile can be obtained. Low-angle XPS can provide improved depth resolutions to about 0.5 nm. This is the top surface to which advancing and receding contact angles in surface tension studies are sensitive.

The elemental compositions of the coatings were calculated from the integrated peak areas and the sensitivity factor for each element (see Table I), which resulted from the carbon 1s, oxygen 1s, nitrogen 1s, silicon 1s and 2p, and phosphorus 2p core-level electrons:

$$C_x = \frac{I_x/S_x}{\sum(I_i/S_i)} \quad (1)$$

where  $C_x$  is the concentration fraction of element X,  $I_x$  is the real integrated area for element X,  $S$  is the sensitivity factor (see Table I), and  $i$  is the total number of elements present in the sample. Coatings were prepared in very thin layers (2–3  $\mu\text{m}$ ) by the dipping of hot-dipped galvanized steel into 5% aqueous dispersions of the phosphated and siloxane-modified polyurethanes and 1 h of drying at 60°C. Samples (1 cm  $\times$  1 cm) were cut and loaded into the Quantum 2000 Intro chamber (Physical Electronics, Eden Prairie, MN), which was then evacuated. Narrow spectra of the samples were recorded with a Quantum 2000 scanning ESCA microprobe (PHI). The source of the X-rays was monochromated Al K $\alpha$  (1486.6 eV; 15 kV). Quantitative data were calculated from the peak areas for each element. Depth distributions were obtained by changes in the takeoff angle from 5 to 90°. For information on depths greater than 70 Å, samples were Ar<sup>+</sup>-ion-sputtered (2 kV of Ar<sup>+</sup> ions at a sputtering rate of 14 nm/min) for the removal of approximately 30 nm of the top surface (although some polymer degradation might have occurred). After the sputtering step, narrow spectra of the samples were recorded, and quantitative data were calculated from the peak areas of each element. This was repeated several times so that a depth profile could be obtained.

## RESULTS AND DISCUSSION

### DCA studies

It has long been known<sup>6</sup> that the surface composition of a multicomponent polymer may differ substantially

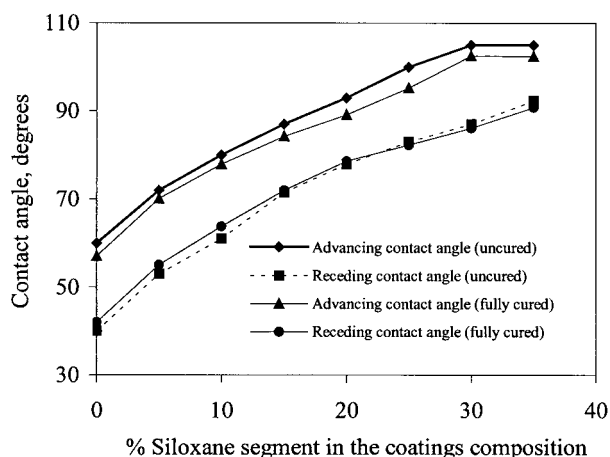
TABLE I  
Sensitivity Factors of the Elements  
in the Coating Composition<sup>5</sup>

Element	Sensitivity factor
Carbon (C1s)	0.314
Oxygen (O1s)	0.733
Nitrogen (N1s)	0.88
Silicon (Si2p)	0.368
Phosphorus (P2p)	0.525

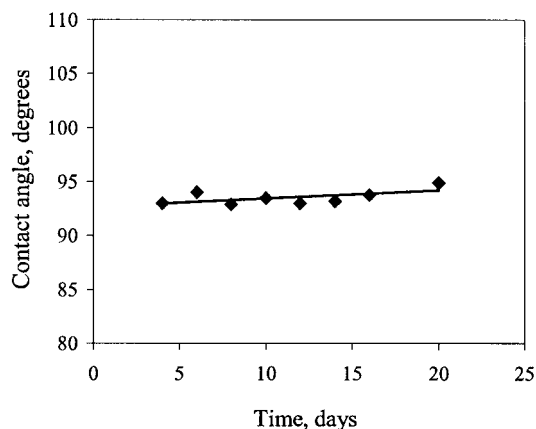
from the bulk composition. This phenomenon is associated with the surface energy, the surface being enriched with lower energy components. The effect of the polysiloxane segment in crosslinked and uncrosslinked coatings on the wettability of the coatings is shown in Figure 2.

Both the cured and uncured coatings showed an increase in the advancing and receding contact angles with an increase in the polysiloxane segment concentration in the film. The curing of the coatings led to a slight decrease in the advancing contact angles. This was due to chain entanglements caused by network formation and the presence of the rigid melamine ring in the crosslinking agent. This ring structure hindered the free rotation of the siloxane chains to move into the coating-air interface.

When coated on polar surfaces such as metal, poly(dimethyl siloxane) chains in polyurethane coatings change from a random coil to a spread-chain conformation, in which the urethane groups are oriented toward the bulk and the siloxane methyl groups are oriented away from the bulk. The spreading coefficient is high because of the low interchain cohesive energy density of poly(dimethyl siloxane). Consequently, when poly(dimethyl siloxane) contacts high-energy substrates, surface films form readily. The new surface presented by the siloxane methyl groups is of significantly lower energy.<sup>7</sup> The consequences of the free orientation of polymer chains are low cohesive energy density and low surface energy, resulting in poor wetting (high contact angle) of the coatings as the siloxane content increases. It is known that the only polymers that have lower surface energy than poly(dimethyl siloxane) are some of the highly fluorinated polymers, such as poly(hexafluoropropylene), and that the low surface energy of poly(dimethyl siloxane) is maintained not only in coatings but also when it is



**Figure 2** Advancing and receding contact angles of water on cured and uncured phosphated and siloxane-modified polyurethane dispersion coatings.



**Figure 3** Effect of atmospheric conditions on the wettability of phosphated and siloxane-modified polyurethane coatings.

reinforced with fillers of different surface-energy values.<sup>8</sup>

The poor wettability of the coating surfaces as a function of the siloxane chains, as previously discussed, showed consistency with time under standard atmospheric conditions, as presented in Figure 3. The phosphated and siloxane-modified polyurethane coatings were made from hydrophilically modified carboxylic acid comonomer, which had particle sizes below 70 nm.<sup>2</sup> The coatings derived from water-dispersible polymers were, therefore, expected to be hydrophilic and have lower water contact angles. However, the coatings had poor wetting properties because of the assembly of silicone-rich components on the surface, and the polar and hydrophilic components were buried in the film. The driving force that caused the burying of hydrophilic groups in the siloxane-based polyurethane coatings, as shown by the poor wettability, was the thermodynamic requirement of minimizing the interfacial tension of the coatings.

Under certain conditions, the buried hydrophilic and polar groups should, because of thermodynamic requirements, be reversed when the surrounding phase is changed.<sup>9</sup> For this reason, coatings were immersed in a 5% aqueous solution of ammonium chloride for 15 days, and contact-angle measurements were performed 15 min after the samples were taken from the solution, so that a time-dependent hydrophobic recovery would be avoided. As shown in Figure 4, significant decreases in the water contact angles were observed after the samples were exposed to an ionic solution of ammonium chloride for 15 days. The decrease in the contact angles with immersion in the aqueous ammonium solution was thought to be due to the leaching out of some of the loosely attached, low-surface-energy components or to the detachment of some hydrophobic moiety through a chemical reaction with the solution.

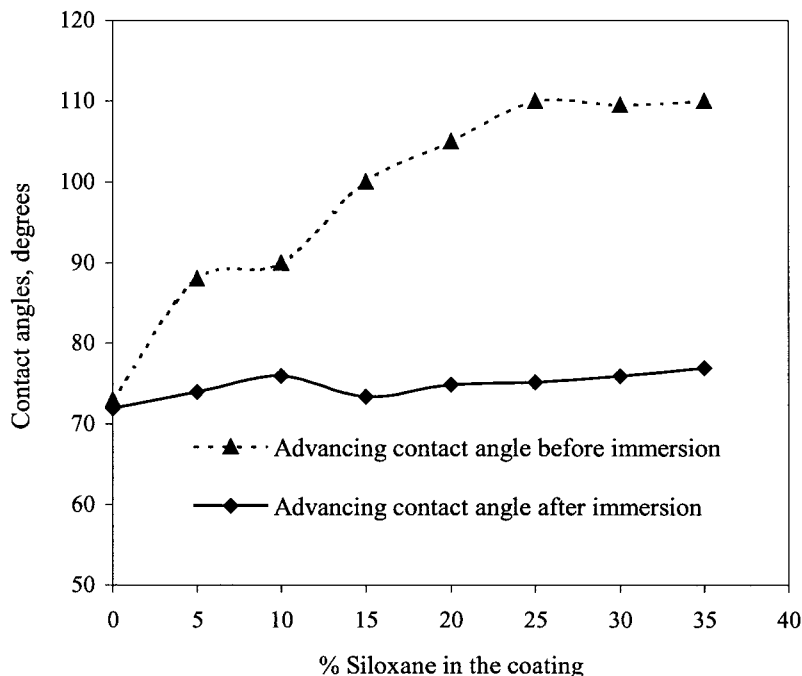


Figure 4 Effect of the coatings being soaked in an ammonium chloride solution on the contact angle.

In an effort to prove this assumption, we rinsed the same samples with deionized water and kept them at 30°C. The contact angles were then measured as a function of time. The hydrophobicity completely recovered, as shown in Figure 5. The cyclic loss and recovery of the DCAs led to the rather fundamental finding that the change in the contact angles was due to the surface dynamic change of the self-assembling coatings rather than the previously mentioned assumption of leaching or detachment.

The results in Figures 4 and 5 highlight the rotational and diffusional migrations of the hydrophobic

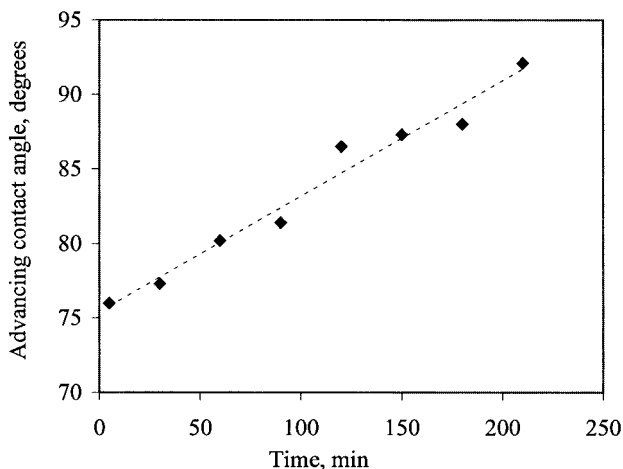
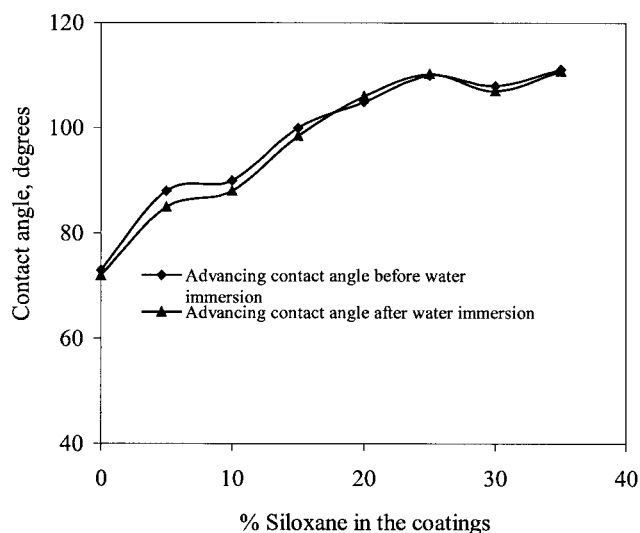


Figure 5 Hydrophobic recovery of phosphated and siloxane-modified polyurethane self-assembling coatings (10% siloxane in the coatings) at 93 and 76° before and after immersion, respectively

siloxane chains away from the polar liquid/film surface upon immersion in an ammonium chloride solution. Such migrations could be anticipated because the amorphous nature of the coatings gave the coatings a high-gloss finish and a low glass-transition temperature, the overriding criterion for metal coatings such as coil coatings being film flexibility. The migration of the chains to and away from the surface may, however, be hindered by the presence of the crystalline phases in the polymer, as well as crosslinking. For plasma fluorine-treated poly(ethylene terephthalate) and nylon 6 immersed in water, Yashuda et al.<sup>10</sup> reported a decrease in the diffusion-controlled hydrophobic recovery as crystallinity increased.

Macromolecules at a polymer surface have a high degree of freedom in determining their conformation according to the immediate neighboring phase. The considerable mobility and specific arrangement of functional groups of macromolecules at a surface are dictated by environmental conditions to which the surface is exposed. Consequently, changes in environmental conditions, such as immersion in ionic solutions, can cause considerable changes in the surface characteristics in comparison with the characteristics evaluated under atmospheric conditions. The effect of water on the surface dynamic nature of the coatings was also studied by the immersion of the coatings in distilled water for 15 days and the measurement of the contact angles 10 min after removal from the distilled water. No quantifiable changes in the contact angles of the coatings were observed, according to the disappearance and reappearance of the siloxane groups on



**Figure 6** Effect of water immersion on the advancing contact angle of phosphated and siloxane-modified self-assembling polyurethane coatings immersed for 15 days in distilled water and dried under ambient conditions for 10 min.

the coating–air interface, as shown in Figure 6. Many workers<sup>11–13</sup> have reported a decrease in contact angles for some polymers when they were brought into contact with water. The better wettability of polymer surfaces after exposure to water in the cited literature<sup>11–13</sup> was mainly due to the use of water-soluble polymers and highly hydrophilic surfaces such as poly(hydroxy ethylmethacrylate). In this study, the coatings were made hydrophilic by the neutralization of the pendent carboxylic acid with volatile amines; once the coatings were cured, the amines were lost, and the polymer was no longer highly hydrophilic and wettable by water. In addition, the polar groups were buried under the self-assembling surface. Therefore, the contact angle of water on the surface of the phosphated and siloxane-modified self-assembling polyurethane coatings depended on whether the polar moieties of the polymer molecules were oriented toward the air interface or toward the bulk of the solid, not on the total polarity, and the short-range rotational mobility of a polymer molecule had a major influence on the contact angle.<sup>6</sup>

The differences in the wetting behaviors of the coatings after exposure to an ammonium chloride solution can be explained in terms of polarity. When the coatings were in contact with the solution, the polar groups oriented toward the surface. As the polar components diffused into the coating–solution interface, the polar urethane groups were the components that came to the surface and gave better wetting (a lower contact angle) with water. Although the polar groups moved into the outer surface, the urethane groups were hydrolytically stable in the presence of water, and no coating failure was observed.<sup>14</sup>

There has been a growing interest in self-assembling coatings for many applications, particularly antifouling, for the elimination of toxic copper compounds that adversely affect nontargeted organisms in the sea.<sup>15</sup> In an attempt to achieve this, Brady et al.<sup>15</sup> studied self-assembling fluoro-coatings and characterized their fouling properties in seawater. They used DCAs to measure the self-assembling nature of the fluoro-groups before immersion in seawater. However, Brady et al. did not report the DCAs in terms of self-assembly after immersion in seawater. It should be noted from this study that ionic solutions attracted the polar component into the coating–air interface and reduced the contact angle of siloxane-based coatings, and the same may be expected from fluoropolymers.<sup>10</sup>

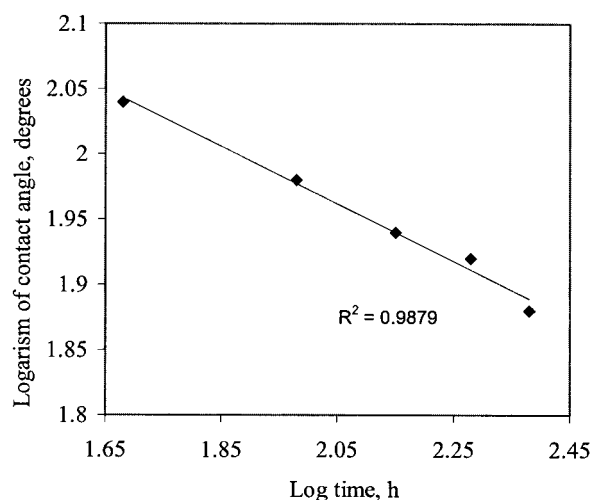
The extent to which self-assembling coatings disappear from the surface during the immersion of the coatings in ionic solutions can empirically be related to diffusion-controlled chemical reactions. The diffusion-controlled reaction parameter in polymer matrices, for which the extent of reaction is proportional to the contact angle of water before and after immersion, has been reported as a parameter to explain the loss of hydrophobicity in contact-angle studies.<sup>10</sup>

For a coating sample immersed in an ammonium chloride solution for time  $t$ , the hydrophobic decay after time  $t$  ( $A_t$ ) is related to the parameter of the original sample before immersion ( $A_0$ ) as follows:

$$A_t = A_0 t^{-k} \quad (2)$$

If we take the logarithm,

$$\text{Log } A_t = \text{log } A_0 - k \text{ log } t \quad (3)$$



**Figure 7** Loss of hydrophobicity in the coatings as a function of the immersion time in an ammonium chloride solution.

The typical disappearance of hydrophobic character, expressed as the logarithm of the contact angle  $\theta$  for the coatings as a function of the logarithm of immersion time  $t$ , is shown in Figure 7. There is a linear relationship with the immersion time. The  $k$  parameter is an indication of the mobility of the molecule away from the surface.

### XPS analyses of the self-assembling coatings

The elemental compositions of the phosphated and siloxane-modified polyurethane dispersion coatings determined at different takeoff angles are presented in Tables II and III.

As can be seen in both tables, phosphorus and nitrogen were not detected in all the samples at lower takeoff angles (5 and 30°), and this indicated that the polar urethane groups and phosphorus were not on the surfaces of the coatings. In Table II, the silicon and oxygen contents decreased as the takeoff angle increased from 5 to 90°. However, the carbon content increased from 5 to 90°. Small amounts of both nitrogen and phosphorus were detected at higher angles (higher depths). The decrease in silicon with depth is an indication of the assembly of the silicon at the very top surface (<15 Å).

The assembly of the silicon can be explained by the oxygen content, which showed a similar trend to that of the silicon content. The decrease in oxygen with the decrease in the silicon content was related to the Si—O—Si bond of the polysiloxane chain. Therefore, as the amount of silicon decreased toward the bulk of the polymer, so did the oxygen. As discussed earlier, the poor wettability of the self-assembling coatings was due to the lower surface tension of the polysiloxane chains, which the XPS results confirmed. It was also mentioned that the polar urethane group accounted for the improved wettability of the coatings after exposure to an ammonium chloride solution. As can be seen in Table II, the urethane groups were not present (no nitrogen) in the surface-sensitive region of

**TABLE II**  
Elemental Composition (%) of Phosphated and Siloxane-Modified Polyurethane Coatings<sup>a</sup>

Element	Takeoff angle			
	5°	30°	60°	90°
Carbon	57.02	60.75	63.00	66.00
Oxygen	24.91	24.48	24.15	20.10
Silicon	18.07	14.77	10.23	10.19
Nitrogen	0.00	0.00	2.33	2.39
Phosphorus	0.00	0.00	0.29	0.32

<sup>a</sup> A 20/80 ratio of polysiloxane macroglycol to phosphated macroglycol was reacted *in situ* with the isocyanate to obtain phosphated and siloxane-modified polyurethane dispersions with 70% soft segment and 30% hard segment.

**TABLE III**  
Elemental composition (%) of phosphated and siloxane-modified polyurethane coatings<sup>a</sup>

Element	Takeoff angle			
	5°	30°	60°	90°
Carbon	51.40	66.00	75.73	78.70
Oxygen	23.12	15.45	13.11	10.00
Silicon	25.48	16.55	3.06	0.20
Phosphorus	0.00	0.00	2.20	4.20
Nitrogen	0.00	0.00	5.90	6.80

<sup>a</sup> The polysiloxane-based polyurethane dispersion was blended into a phosphated polyurethane dispersion.

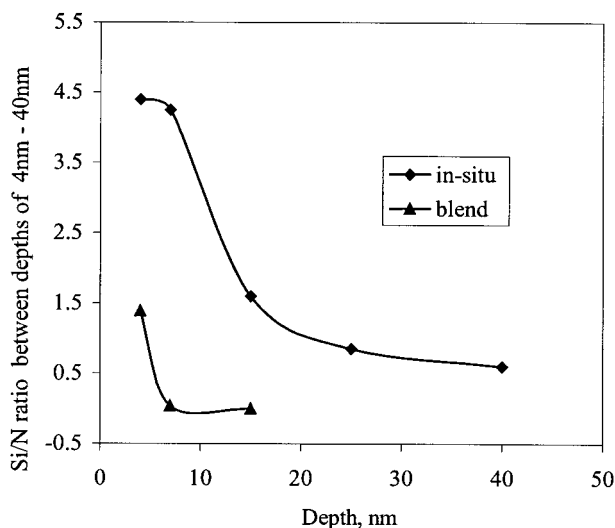
the DCA tests under ambient conditions. Therefore, the polar groups were indeed buried in the bulk until they came into contact with the ionic solution.

The effect of the method of incorporating the siloxane groups into the dispersions on self-assembly is presented in Table III. The siloxane-based polyurethane dispersion was blended into a phosphated polyurethane dispersion, whereas the dispersions described in Table II were obtained by *in situ* polymerization of the siloxane and the phosphated macroglycols with the isocyanate and chain extender. However, both coatings had the same percentage of siloxane groups.

The significant difference between the two coatings can be seen in the silicon content at 5 and 30° in a comparison of Tables II and III. In Table III, a 40% increase in silicon can be observed at 5° with respect to Table II; this indicated that the coatings from the blend dispersions enriched the surface with more silicon than did the coatings from the *in situ* reaction product. The silicon content of the coating prepared from the blend dispersion was close to that of the pure siloxane. In the pure siloxane segment, the silicon percentage was 26.92; for the coating at 5°, it was 25.48%.

The silicon enrichment seen in Table II can be explained in terms of incompatibility and, therefore, phase separation between the segments due to solubility differences between the phosphated polyurethane and the siloxane polyurethanes. Pascault and Camberlin<sup>16</sup> studied block copolymers of poly(dimethyl siloxane) and polyurethanes and found that the solubility differences between the segments were responsible for the silicon enrichment at the film–air interface. Tezuka et al.<sup>17</sup> investigated the wetting properties of poly(vinyl alcohol)–poly(dimethylsiloxane) grafts and found that the air–polymer surface was essentially covered with pure siloxane segments.

The silicon content at different takeoff angles (Table III), however, is explained by the ease with which the siloxane segments move independently of the phosphated polyurethane chains. Polymer chains in a blend move much more freely than those in covalently bonded and crosslinked polymers. For coatings pre-



**Figure 8** Dependence of the Si/N ratio between depths of 4 and 40 nm on the method of incorporating the siloxane chains into polyurethane dispersions.

pared by *in situ* polymerization of the siloxane and the phosphate-containing macroglycols with the isocyanate, the siloxane groups are covalently linked with the whole chain. Therefore, although the silicone chains try to move to the outer surface, they will be restricted by the covalent bond together with the rest of the chain that contains phosphate. Therefore, when the depth is increased, the silicon content of the *in situ* reaction is substantially higher than that of the blend dispersion, for which the silicon is almost negligible (cf. 0.2 and 20.19% at 90°)

The detection of the nitrogen 1s electrons at a binding energy of 400 eV indicates the presence of the urethane hard segments because the urethane groups are the only nitrogen-containing functional groups. The silicon 1s and 2p electrons at 150- and 102-eV binding energies, respectively, are only from the polysiloxane groups. The carbon and oxygen 1s electrons are from all the segments (the polyester, the urethane, and the siloxane). Therefore, the ratio of silicon to nitrogen was used to characterize the surface. The results of the ratio of silicon to nitrogen versus the depth are presented in Figure 8.

The Si/N ratio of the coatings prepared from the *in situ* reaction remained high, even at depths greater than 40 nm, and the Si/N ratio for the blend dropped to zero after a depth of 9 nm. Because nitrogen was not observed at the lower takeoff angles (Si/N becomes meaningless), Figure 8 shows the values of the Si/N

ratios obtained for 60 and 90° and those obtained via sputtering to depths of 40 nm.

Sputtering was done to obtain a relative indication of the elemental composition. The exact values of each element may be higher than the values obtained here because some degradation can take place due to the high energy used to sputter the samples. Nevertheless, the elemental composition values in Tables II and III were sufficient to conclude the self-assembly of the coatings without sputtering.

## CONCLUSIONS

Self-assembling phosphate and siloxane-containing polyurethane dispersion coatings were evaluated at the coating–air interface. The coatings showed poor wettability when the amount of the siloxane in the polyurethane was increased. Curing with melamine resin decreased the advancing and receding contact angles because of the rigid structure of melamine and the crosslinking, which hindered surface rearrangement. The coatings lost their self-assembling properties when exposed to ionic solutions because of surface dynamics, but this could be reversed when they were taken out of the solutions. XPS and DCA studies showed the self-assembling nature of the coatings.

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