Adhesion Properties of Phosphate- and Siloxane-Containing Polyurethane Dispersions to Steel: An Analysis of the Metal–Coating Interface

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ABSTRACT: Polyurethane dispersions containing phosphate and siloxane groups in the main chain were investigated as possible self-assembling metal coatings. Improved adhesion of the polymer to the metal was observed because of the formation of an insoluble metal phosphate layer at the metal–coating interface. The neutralizing amine of the dispersions affected the formation of this metal phosphate, and the metal phosphate formation was dependent on the curing temperature and boiling point of the amine used for neutralization. A crosscut comparative study of adhesion proved that the phosphate-containing coatings had better adhesion because of the formation of ionic bonds at the metal–coating interface. A solid-state adhesion prediction method based on thermodynamic considerations was used. The results of the solid-state adhesion method correlated well with that obtained from the crosscut adhesion test method. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 900–907, 2003

Key words: polyurethanes; adhesion; X-ray

INTRODUCTION

Phosphating is a widely used metal-treatment process for the surface finishing of ferrous and nonferrous metals. The surface-phosphating treatment of steel before the application of coatings or adhesives, for improving adhesion and inhibiting corrosion, is a conventionally used industrial practice. The phosphate conversion coating results in a nonconductive layer of metal phosphate in its crystalline form that insulates the metal from corrosion and provides enhanced adhesion for subsequent coatings. The quality of finish required by industry determines the degree to which the pretreatment and phosphating are carried out. For example, the phosphate conversion coating (pretreatment) of zinc surfaces yields insoluble hydrate films of $Zn_3(PO_4)_2 \cdot 4H_2O$. In a traditional multistep process, the metal surface is cleaned several times and by several means, phosphated, and sealed before it is dried with hot air and is ready for painting. Because industrial phosphating does not cover 100% of the metal surface,[1] the unphosphated area becomes suspect to corrosion, and sealing is usually done with a chromate solution. The use of a chromate pretreatment for aluminum or the use of it as a seal for phosphated metals is, however, expected to be banned (in some countries it is already banned) because hexavalent chromium (Cr^{6+}) is a known carcinogen.[2] In most commercial treatment lines, oxidizing agents and accelerators are added for faster production and increased line speed. The disposal of all these toxic wastes is becoming a serious problem. Therefore, the idea of combining the metal phosphate and the organic coating in a single process, by means of phosphorus-containing polymers, is a novel idea that could eliminate the existing multistep process and health threat of the wastes.

The inclusion of phosphoric acid groups in a polymer chain can impart interesting properties to the polymer. These include reduced flammability,[3] increased adhesion to metals,[4] metal-ion binding characteristics,[5] and greater solubility in polar solvents and alkali.[6,7] Phosphoric acid-containing polymers with added carboxylic groups are also used for ion exchange and scale inhibition and as water-soluble base coats for metals. The extent of modification of the properties of the polymers depends on the number of phosphoric acid groups present. Phosphorus-containing compounds can be incorporated into a polymer in two ways: the unreactive phosphorus compounds can be blended with the polymer during compounding, or the phosphorous compound can be chemically bonded and become an integral part of a polymer. The second method is the better method because polyurethanes that contain phosphorus that is not chemically bonded to the main chain are susceptible to the loss of

the phosphorus compound by evaporation or leaching during storage.

In this article, we report the adhesion properties of the phosphate- and siloxane-containing polyurethane dispersions through the formation of a metal phosphate at the metal–coating interface.

EXPERIMENTAL

Polyurethane dispersions containing phosphate and siloxane groups on the main chain were synthesized as described previously.[8,9] Hot-dipped galvanized steel panels were obtained from ISCOR (Vereeniging, South Africa).

Characterization

Energy-dispersive X-ray spectrometry (EDXS)

EDXS was used to characterize the self-assembly at the metal–coating interface and to study the formation of the metal phosphate by the polymer and the untreated metal. Samples for EDXS analysis were prepared by the dipping of a metal plate into a 5% aqueous dispersion of phosphated and siloxane-modified polyurethane and drying at 75°C for 12 h *in vacuo*. The coatings did not contain any crosslinker, and the dispersions used here were linear polymers that were soluble in tetrahydrofuran (THF). As a result, the coating was also soluble in THF. The metal phosphate so formed was evaluated after the coating layer was fully etched by THF for 6 h. To prove the solubility of the polymer in THF after it dried at 75°C, we kept a separate sample in an aluminum dish for 12 h at 75°C; it was then redissolved in THF and filtered. No gel formation on filtration was detected. The EDXS analysis of the interface was done with a Topcon ABT-60 Link model 5079 with a 25-kV beam equipped with a 0.008-Be window (Topcon Technologies, NJ). The detector area was 10 mm^2. The data were analyzed and plotted with an AN 10000 software X-ray analyzer.

Dynamic contact angle

Solid-state adhesion was evaluated with a Cahn DCA-322 dynamic-contact-angle analyzer (Cahn Instruments, Madison, WI) operating at 25°C and at a velocity of 100 μm/s. Hot-dipped galvanized steel panels were cut to 1.5 cm × 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 suspended in a curing oven and cured at a peak metal temperature of 230°C for 20 s.

Atomic force microscopy (AFM)

AFM images of the surfaces were recorded on an Explorer TMX 2000 atomic force microscope (Topome-
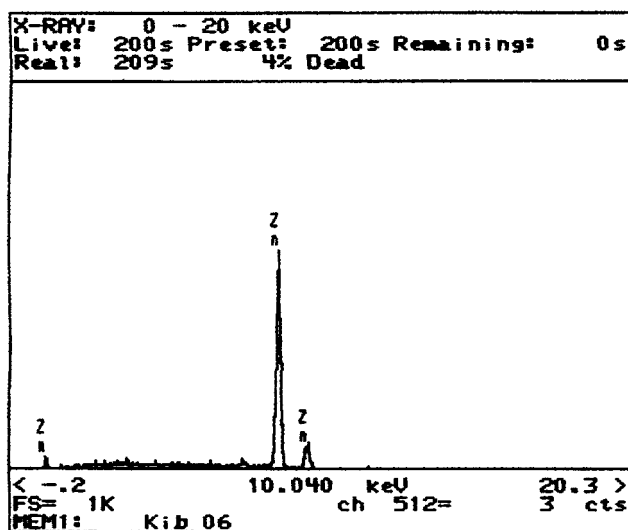

Figure 1 EDXS spectrum of the bare, hot-dipped galvanized steel.

trix Inc., Santa Clara, CA) with a silicon tip (high-resolution) at a force constant of 30–80 N/m in the noncontact mode.

Crosscut adhesion (tape adhesion)

For a crosscut adhesion test, a lattice pattern with 12 cuts in each direction was made to the film. Care was taken to ensure that each cut was made deep enough to reach the metal substrate. Each resulting lattice (square) was 1.5 mm × 1.5 mm. A pressure-sensitive tape was applied over the lattice and then removed at an angle of 180°. This adhesion test is based on ASTM D 3359-87. It is most useful in providing a relative rating of adhesion for a series of coated panels exhibiting significant differences in adhesion. By this method, any flaking, detachments at intersections, and removal of the square cuts with the tape can be investigated.

RESULTS AND DISCUSSION

EDXS

To ensure that the formation of the metal phosphate on the hot-dipped galvanized steel surface was from the phosphated and siloxane-modified polyurethane coatings and not from any previous treatments, we needed to obtain the EDXS spectrum of the bare metal as a reference. Figure 1 shows the EDXS spectrum of the bare, hot-dipped galvanized steel. Its only peaks are those of zinc, as labeled by the instrument.

Figure 2 shows the EDXS spectrum of the metal–coating interface after it was dip-coated with the phosphated and siloxane-modified polyurethane dispersion and etched with THF. The appearances of zinc at the principal emission line of 8.60 keV and of phos-

phorus at 2.02 keV in the energy-dispersive spectrum indicated that insoluble zinc phosphate was formed at the interface. (Note that the value of 10.04 keV in Figures 1 and 2 is the value of the cursor from the instrument and not the principal emission line for zinc.) The high peak intensity of phosphorus with respect to zinc in the same sample and identical counts (200 counts) indicated the thickness of the phosphate layer. Very thick crystalline metal phosphate layers are, however, not required for applications that require flexibility. Some microcracking of the phosphate layer was observed, by others, underneath a flexible clear coil coating when a highly pretreated metal was subjected to 180° bending (0 bending).[10]

However, when the coating was prepared from a low-phosphate-content polyurethane dispersion, EDXS peaks were obtained with a lower phosphorus/zinc peak ratio, as shown in Figure 3. These results at the interface indicate that when the phosphated polyurethane dispersions were applied on a clean metal, such as galvanized steel, the phosphoric acid groups diffused to the metal and assembled at the interface by forming metal phosphate.

Effect of the neutralizing base on the formation of insoluble metal phosphate

The polyurethane dispersions described in this study were made hydrophilic and dispersible in water by the neutralization of their pendent carboxylic acid groups with tertiary amine.[8] Residual amine retention in the coating film after the drying process was, therefore, expected. Retained amines have been known for some time to affect surface coating properties. For instance, Wicks and Chen[11] and Ferrell et al.[12] reported amine transesterification with a melamine
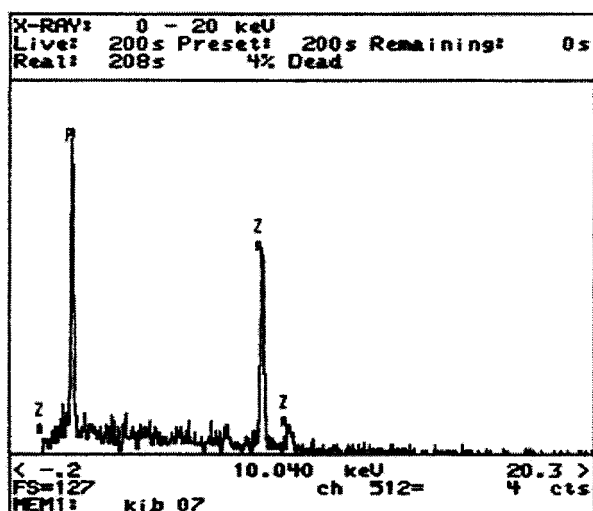

Figure 2 EDXS spectrum of the metal interface after dip coating with the phosphated and siloxane-modified polyurethane dispersions.
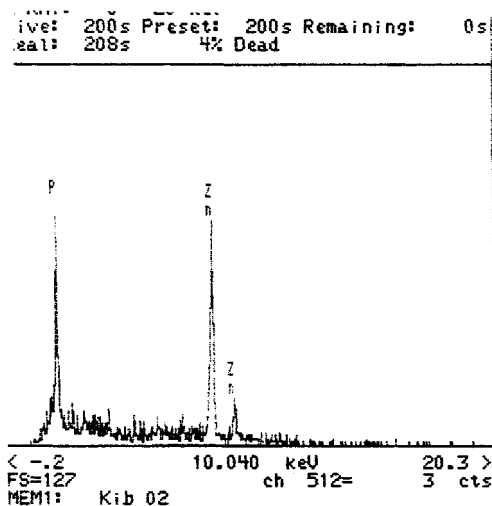

Figure 3 Zinc phosphate formation from phosphated and siloxane-modified polyurethane dispersions (low content of phosphorus).

crosslinker when amino alcohols were used as neutralizing bases for water-dispersible polymers. A drastic reduction in the dynamic mechanical properties of the melamine-cured polyurethane dispersions, when high-boiling amino alcohols were used as neutralizing bases, was reported by Mequanint.[13] The aforementioned references describe the undesirable properties of the amines used for neutralization. Therefore, the neutralizing base may also have an effect on the formation of metal phosphate at the metal–coating interface.

The effect of the neutralizing base on the metal phosphate formation is supported by a comparison of Figures 2 and 4. In Figure 2, the neutralizing amine is triethylamine, and in Figure 4, it is diethanolamine. An EDXS analysis of the metal–coating interface of the galvanized steel coated with dispersions neutralized by diethanolamine revealed no phosphorus peak at 2.05 keV, and only peaks corresponding to zinc were identified.

The reason for the phosphorus not being detected was the complexing effect of the neutralizing amine. In the metal phosphating process, the functional groups of the polymer involved were P=O and POH. Figure 5 shows the Fourier transform infrared (FTIR) spectra of the phosphorus-containing macroglycol used to synthesize the polyurethane dispersion. Only the macroglycol component (instead of the polyurethane copolymer) was measured to avoid any overlapping peaks due to the additional functional groups from the silicone and urethane.

Figure 5 shows two bands at 1005 and 1041 cm^{-1}, which are the P=O stretching vibration, and an absorption at 1168 cm^{-1}, which indicates the aliphatic nature of the P=O stretching[14] (because the monomer used was aliphatic). A medium-strength absorption
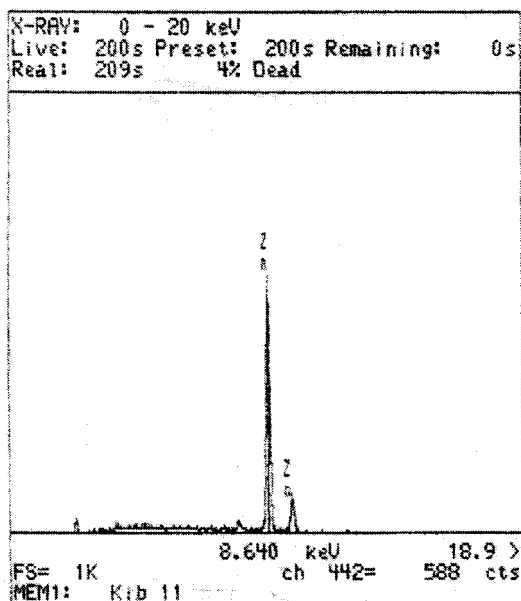
Figure 4 EDXS spectrum of phosphated and siloxane-modified polyurethane coatings showing the effect of diethanolamine as a neutralizing base on the formation of metal phosphate.

can be observed at 1610–1700 cm^{-1} for the P=O(OH) groups.[15] The hydrogen-bonded phosphoryl (P=O) group has a characteristic absorption in the region of 1250–1260 cm^{-1}.[15]

The first step in the formation of the insoluble metal phosphate was the dissociation of the P—OH groups into PO^{-} ions and the reaction with the metal. Second, the resulting metal phosphate layer had to be crystalline. Both the dissociation and crystallization processes required water.[16] The phosphated polyurethane

dispersions had an added advantage because the solvent was water. The final important point here is the pH of the solution, which had to be acidic for metal phosphate formation. Therefore, for metal phosphate formation, the coating composition had to be slightly acidic, if not strongly acidic. This means that the neutralizing amines that existed in equilibrium with the free acid and free amine had to be dissociated:

$$R\text{–}COO^{-} + HNR_3^{+} \rightleftharpoons R\text{–}COOH + NR_3$$
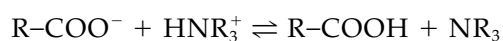
At drying temperatures of 75°C *in vacuo*, triethylamine was likely to dissociate and evaporate because of its low boiling point in comparison with that of diethanolamine. The undissociated amines acted as complexing agents for the P—OH groups, and the coating film remained alkaline. Therefore, crystalline metal phosphate at the interface could not be formed for diethanolamine and during the etching process by THF; the entire coating film was dissolved, and no phosphorus was detected by EDXS at the metal interface. Therefore, when the neutralizing amine had a lower boiling point and a low basicity, it dissociated at a lower temperature and favored metal phosphate formation. [In fact, for coatings intended for use in coil coatings, as long as the curing proceeds thermally, most amines dissociate, and the coatings become acidic because of the high curing temperature (a peak metal temperature of 220°C in most cases) required.] Finally, the acidity of the coatings upon amine dissociation generated carboxylic acids, which acted as weak catalysts for the melamine crosslinking, as described in a previous study of polyurethane dispersions.[13]
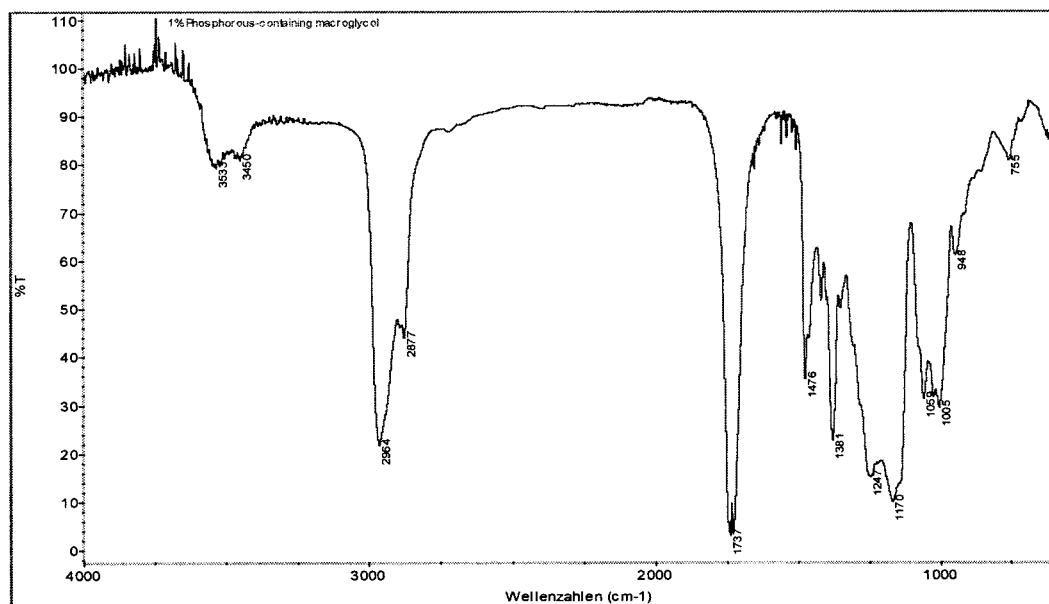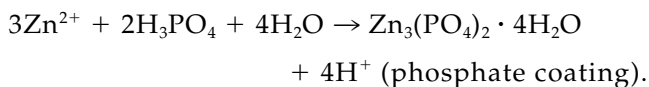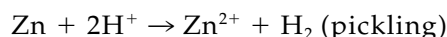

Figure 5 FTIR spectrum of a phosphorus-containing macroglycol.

It was concluded from the EDXS studies that the formation of the insoluble metal phosphate at the metal–coating interface was evidenced by the appearance of a phosphorus peak at 2.02 keV and of a zinc peak at 8.64 keV. The phosphate groups were successfully assembled under favorable conditions at the metal–coating interface. The nature of the metal phosphate depended on the temperature required to dissociate the amine. Silicon was not detected at the interface, and this proved that the silicone-rich components assemble at the coating–air interface and not at the metal–coating interface as expected (discussed later).

Crosscut adhesion

The measurement of the adhesion of a coating is particularly difficult because of the lack of suitable handles for applying the forces necessary to remove a coating layer from its substrate.[17] For this reason, adhesion tests in the coating industry are usually done along with tests of several other properties at the same time, and this makes the adhesion component difficult to isolate.

In a comparative crosscut adhesion test of polyurethane coatings containing phosphate with polyurethane coatings that did not contain phosphate, the former showed improved adhesion properties. On the reverse impact of the crosscut lattices, with a 1.8-kg mass from a height of 1 m, there was no flaking or delamination of the small squares (1.5 mm × 1.5 mm). In comparison, the coatings that did not contain phosphate flaked more than 25%. A possible explanation for the significantly improved adhesion of the modified urethane was the interaction of the phosphoric acid groups of the polymer with the zinc layer of the steel. This interaction could be expected to occur in a way similar to that of a commercial pretreatment. Immersion of the metal in a solution of zinc phosphate in the presence of phosphoric acid is often used to pretreat steel coils:[18]

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \text{ (pickling)}$$

$$3Zn^{2+} + 2H_3PO_4 + 4H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O$$
$$+ 4H^+ \text{ (phosphate coating)}.$$

Hopeite, a mineralogical term, is used to denote the process of zinc phosphate conversion coating. The functional groups that can possibly interact on the metal to produce a metal phosphate layer are P—OH, P—O$^-$, and P=O. The dissociated P—O$^-$ from the polymer can form the ionic bond of P—O$^-$—Zn^{2+} with the metal and is stronger than the P=O/metal bond that is an induced dipole.[19] The strong adhesion of this coating suggests an acid–base interaction by

the zinc layer of the metal and the polymer-chain phosphoric acid groups to form P—O$^-$/Zn^{2+}, rather than an induced dipole interaction of the P=O/M complex type.

A coating composition in which the phosphate groups are chemically bonded to the polymer component and which improves the adhesion and forms a metal phosphate has not been reported. The simultaneous phosphating of metals with a phosphatizing agent as an additive in paint has, however, been reported.[20,21] Here the phosphatizing agent must have a dual role. First, it must diffuse onto the metal interface and become bonded; second, it must react or associate with the polymer to form linkages with good adhesion.

Adhesion of polyurethane coatings to steel based on thermodynamic surface matching

In surface coatings, with the exception of powder coatings and ultraviolet-curing coatings, paints are supplied in suitable carrier solvents. Consequently, the interpretation of wetting is difficult because of preferential adsorption. Further complications arise because the solvents used to dilute the paint are of different molecular species, with different adsorption properties.[22] The lower surface tension of the solvent compared with that of the actual polymer will result in instantaneous preferential adsorption of the solvent to the metal interface, and it may appear as if the contact angle is zero or at least near zero. As the solvent evaporates during the curing or drying, wetting can change because of the multiple attachments of which polymers are capable. Therefore, a more systematic method of thermodynamic surface matching to the solid substrate, to exclude solvents, was used to study adhesion. This was based on measurements of the advancing and receding contact angles of both the solid polymer and the solid metal. If a series of randomly chosen probe liquids (see Table I) of known surface tensions are used to wet the polymer and the metal independently and the hysteresis graphs are plotted, adhesion between the two surfaces can be predicted by visual comparison.[23] From thermody-

TABLE I
Surface Tensions of Probe Liquids Used for Thermodynamic Matching of Surfaces

Liquid	Surface tension (N/m)
Water	72.8
N-Methyl pyrollidone	40.7
Dimethylformamide	37.3
Propylene glycol monomethyl ether acetate	28.2
o-Xylene	30.1
Hexane	18.7
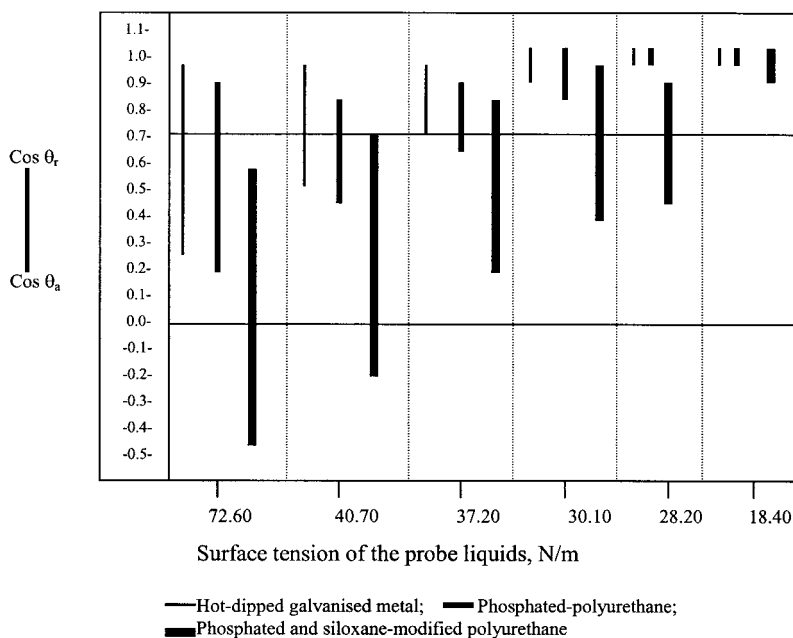
Figure 6 Hysteresis spectra of the hot-dipped galvanized steel and the phosphated coatings with and without siloxane.

namic compatibility considerations, those surfaces that have similar hysteresis spectra correlate with better adhesion because solids with similar hysteresis graphs have similar surface chemical interactions.

The results of the contact-angle study are shown in Figure 6. Each graph represents one spectrum for each liquid. The bottom of each spectrum is the cosine of the advancing contact angle (cos θ_a), and the top of each spectrum is cosine of the receding contact angle (cos θ_r). In this contact-angle study of the phosphated and siloxane-modified polyurethane coatings, only two immersions were performed, to avoid swelling and, therefore, large hysteresis. The Y axis is the cosine of the contact angle. The X axis is an ordered list of probe liquid surface tensions. The length of each spectrum is the measure of the contact-angle hysteresis.

There is a close similarity between the spectra of the metal and the phosphated polyurethane, confirming that the steel surface and the coating film were thermodynamically compatible and indicating good wettability between the polymer and the metal.

The effect of the self-assembling silicone coatings on the surface energies of a coating is also shown in Figure 6. When we compare the spectra of the phosphated and siloxane-modified polyurethane with the phosphated polyurethane and the bare metal, we see that the surface of the phosphated and siloxane-modified polyurethane coatings was drastically modified. For all the probe liquids used, both θ_a and θ_r decreased, and this indicated the poor wettability of the surface of the phosphated and siloxane-modified polyurethane coating. The reduction in the surface energy of the coating layer, due to the self-assembly of the coatings, resulted in poor wettability for all the

solvents used as probes. This was not surprising because the contact-angle measurements were highly sensitive to the chemical characteristics of the outermost part of the solid surface. The solvents used here were carefully chosen to cover almost all surface tensions used in the coating industry, ranging from 18 to 72 N/m. The only exceptions in Figure 6 are the hysteresis graphs of the phosphated and siloxane-modified polyurethane coating when hexane was used as the probe liquid. Here, an improved wetting of the coating was observed because of the low surface tension of hexane. The surface tension of hexane is below the critical surface tension of poly(dimethyl siloxane), and from the critical surface tension concept, hexane is expected to wet poly(dimethyl siloxane). Although in Figure 6, the thermodynamic surface matching between the metal and the phosphated and siloxane-modified polyurethane dispersion coatings is far from close, the self-assembly of the phosphate groups at the metal interface and the self-assembly of the siloxane at the air interface were the important factors resulting in the observed good adhesion.

Contact-angle hysteresis

Contact-angle hysteresis, the difference between the equilibrium value of θ_a and the equilibrium value of θ_r, is a frequent observation in dynamic-contact-angle studies. In this study, θ_a was much greater than θ_r for the high-surface-tension liquids, such as water, whereas for the lower surface tension liquids, θ_a approached θ_r. In some cases, θ_a was equal to θ_r. However, $\theta_a = \theta_r$ does not mean that the contact angle was zero as $\theta_a = \theta_r$ occurred at $\theta > 0$.[24]
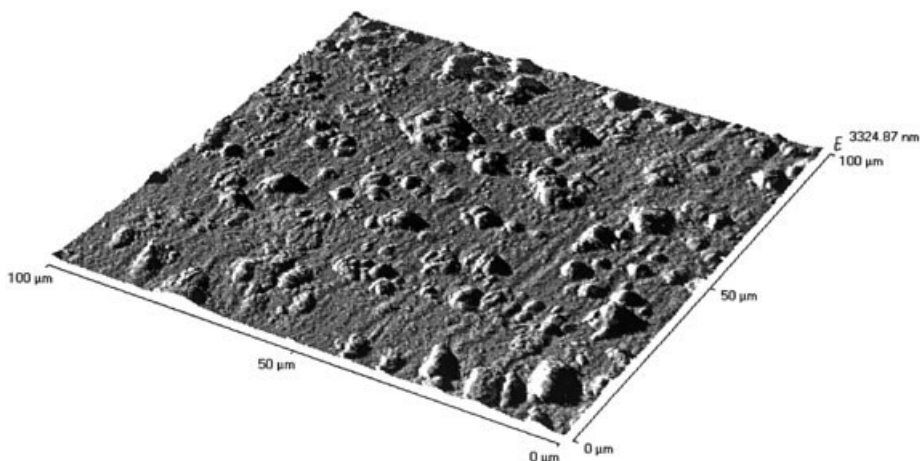
Figure 7 Three-dimensional AFM image of a galvanized steel surface showing surface roughness.

The hysteresis of the bare metal was caused by roughness and heterogeneity, as evidenced by AFM (Fig. 7). A crystalline metal has a high molecular or atomic density and, therefore, different surface free energies. The structure of the grain boundary at the zinc layer had a profound effect on hysteresis. Because of this grain difference, the surface was rough and heterogeneous and affected the wetting property. On heterogeneous surfaces, θ_a is sensitive to the less wettable surface (low surface energy), whereas θ_r is more sensitive to the more wettable part. This means that θ_a directly shows the surface energy condition, whereas θ_r shows the surface energy condition of the already wetted surface.[25]

Surface roughness was not the primary cause of hysteresis for the coatings in this study because AFM (Fig. 8) did not reveal any rough surface of the coatings that could cause the observed large hysteresis.

Time-dependent dynamics and swelling of the polymer surfaces were also assumed to be the primary causes of contact-angle hysteresis.[26] However, the coatings prepared did not swell during contact-angle studies, as evidenced by the smooth force reading during immersion and withdrawing. Furthermore, the self-assembly property of the coatings did not change with time under normal conditions, as reported in our previous publication.[27] For the coatings, only surface heterogeneity would explain the hysteresis differences shown in Figure 6. The increase in the contact angle with the siloxane content in the coating formulation[27] indicates that the top surface was not fully enriched with the low-surface-tension siloxane (at least up to 25% siloxane), and some polar groups might have been present in patches. Therefore, θ_a sees the siloxane–air interface, whereas the receding angle sees the polar patches at the interface, and large hysteresis is obtained.

CONCLUSIONS

The adhesion properties of phosphate- and siloxane-containing polyurethane dispersions were investi-
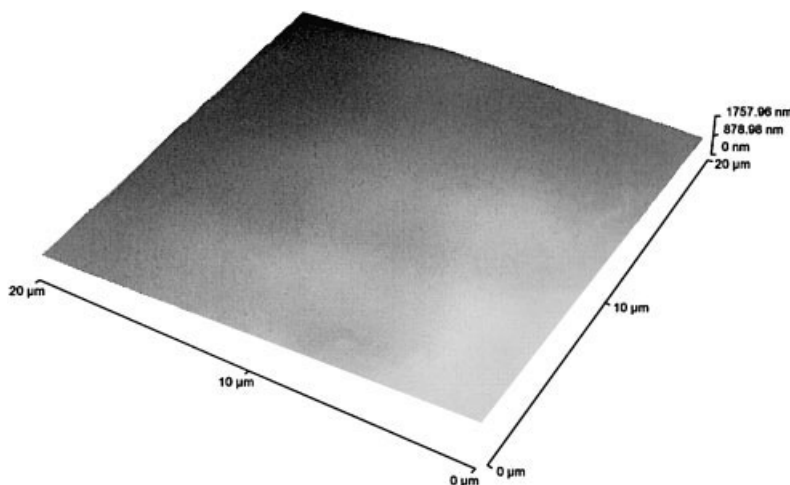
Figure 8 Three-dimensional AFM image of a coating on galvanized steel showing a smooth surface.

gated. Metal phosphate formation at the metal–coating interface was made possible. The increased adhesion of the coatings was due to the formation of ionic bonds between the metal and the phosphate groups of the coating component. The formation of the insoluble metal phosphate was dependent on the neutralizing amine used to disperse the polyurethane in water. Thermodynamic surface matching of the wetting forces on the metal and polymer surfaces revealed the self-assembling tendency of the coating, in which the phosphate was diffused into the metal–coating interface and the siloxane component was diffused into the coating–air interface. This self-assembling property gave high-contact-angle hysteresis due to surface heterogeneity. This phenomenon also explains the excellent wetting (phosphate-induced), smooth surface (siloxane-induced), strong adhesion (metal phosphate-induced), and the material toughness (bendability and adhesion) created by the phosphated and siloxane-modified polyurethane.

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