rosion problem. The case provides a prime example—representing no more than exercises in the study of electrochemical phenomena employing combinations of metals and environmental conditions chosen mainly to facilitate experiments for the convenience of the investigator and to enable him to make use of equipment and experimental techniques with which he is familiar or which are currently in vogue." (Corrosion, 33 (2), 76 (1977).)

An important subject which was to have been presented is entitled, "What We Do Not Know about Corrosion". Unfortunately, the author, Dr. David A. Vermilyea was not able to participate. This message is recorded in two publications: *Mater. Sci. Eng.*, **25**, 29–34 (1976), and *Phys. Today*, **29**, No. 9 (1976). Each is a powerful spring-board preface to launch a systematic future.

A value-added feature, following the two-day lecture session, was a workshop conducted on the following day to provide answers to the question "What Can Be Done about It?" Here the authors of the 20 papers were invited to engage in dialogue with the audience. Five discussion leaders presided to introduce separate subject segments to stimulate discussion, as follows: K. Hamann, interfacial reactions; C. Kumins, transport through membranes; T. Fort, Jr., surface energetics; J. Patterson, corrosion inhibition; J. Gardon, summary and future plans.

We acknowledge credit, with thanks, to authors, discussion leaders, and the audience.

# Acid–Base Interactions in Polymer Adsorption

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PMMA, a basic polymer, is found to adsorb strongly from neutral organic solvents onto the acidic silanol sites of a silica filler, providing 50 times more adsorption per unit area than is observed on the basic surface of a calcium carbonate filler. Acidic solvents tend to solvate and neutralize the basic groups of the polymer and will prevent adsorption if the solvent is more acidic than the surface sites of the acidic filler; the acidity of competing solvents is a measure of the acidity of surface sites. Similarly, basic solvents tend to neutralize the acidic silanol sites of the silica filler and will prevent adsorption if the solvent is more basic than the ester groups of the polymer; the basicity of competing solvents is a measure of the basicity of the polymer. These rules are found to govern both adsorption and desorption. Similar findings resulted with post-chlorinated PVC, an acidic polymer, in adsorption studies with calcium carbonate, a basic filler. Dipole–dipole interactions between these polar polymers and polar adsorbents appear to be negligibly small compared to the acid-base interactions.

### Introduction

The adsorption of polymers from organic solvents onto the surface of inorganic solids obviously involves interactions between polymers and inorganic solids but also must involve interactions between polymers and solvents and between solvents and inorganic solids. Adsorption results only when the interaction between polymer and inorganic solid exceeds the interactions between polymer and solvent, and between solvent and inorganic solid. Meaningful interpretation of polymer adsorption requires understanding of interactions of interfaces and in solution. In this paper we propose a new approach to these interactions, using the correlations of acid-base interactions by Drago et al. (1971) to explain and predict all polar and hydrogen-bonding interactions. This is conceptually and mathematically a very different approach from the widely used equations (appropriate to dipole-dipole interactions) of Hansen (1967) and Kaelble (1970).

# Intermolecular Interaction in Solutions and at Interfaces

Intermolecular interactions in solution have been correlated by regular solution theory (Hildebrand and Scott, 1950), using the solubility parameter ( $\delta$ , the square root of the energy of vaporization per unit volume) as a means of predicting the heat of mixing of solute and solvent

$$\Delta H_{\rm M} \approx \Delta U_{\rm M} = V_{\rm m} \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \tag{1}$$

where  $V_{\rm m}$  is the molar volume of the mixture and  $\phi_1$  and  $\phi_2$ are volume fractions. Similarly, the intermolecular interactions at interfaces have been correlated (Girifalco and Good, 1957) with the surface tensions  $\gamma$  used to predict the work of adhesion

$$W_{\rm A} = 2\Phi \sqrt{\gamma_1 \gamma_2} \tag{2}$$

in which  $\Phi$  was thought to be determined by the molecular volumes. These two approaches both employ the geometric mean of the intermolecular forces within the two separate components to predict the intermolecular forces between unlike components, and there is often serious doubt as to the validity of such an assumption, especially with hydrogenbonded liquids (Bagley and Scigliano, 1975).

In 1961, the senior author (Fowkes, 1962, 1964) proposed that since intermolecular attractions result from several fairly independent phenomena (such as dispersions forces (d), dipole interactions (p), hydrogen-bonds (h), etc.), it is reasonable to separate out such terms in the work of adhesion

$$W_{\rm A} = W_{\rm A}{}^{\rm d} + W_{\rm A}{}^{\rm p} + W_{\rm A}{}^{\rm h} + \dots \tag{3}$$

and in the surface tension

$$\gamma = \gamma^{d} + \gamma^{p} + \gamma^{h} + \dots \tag{4}$$

This principle leads to the widely used equation

$$W_{\mathsf{A}}^{\mathsf{d}} = 2\sqrt{\gamma_1^{\mathsf{d}}\gamma_2^{\mathsf{d}}} \tag{5}$$

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with which interfacial tensions, contact angles, free energies of adsorption, and Hamaker constants were successfully calculated. In confining the use of this equation to dispersion force interactions the geometric mean expression is correct (Fowkes, 1964). There is also some reason to treat dipoledipole interactions separately with the geometric mean expression

$$W_{\rm A}{}^{\rm p} = 2\sqrt{\gamma_1{}^{\rm p}\gamma_2{}^{\rm p}} \tag{6}$$

The interaction energy between two dipoles is  $-2\mu_1^2\mu_2^2/3kTr_{12}^6$ , so if the distance between dipoles  $r_{12}$  is the geometric mean of  $r_{11}$  and  $r_{22}$  of the pure materials, then eq 6 is correct.

The extension of eq 3, 5, and 6 to try to predict hydrogen bonding with a geometric mean expression is quite incorrect, for hydrogen-bond acceptors such as ethers, esters, or aromatics cannot themselves form hydrogen bonds, and therefore  $\gamma^{\rm h}$  is zero for such materials, even though these materials have a large  $W_{\rm A}^{\rm h}$  with hydrogen donors (Fowkes, 1972). Similarly, some hydrogen donors such as chloroform have zero values of  $\delta^{\rm h}$ , but large values of  $W_{\rm A}^{\rm h}$ .

Zisman's extensive series of contact angle measurements of organic liquids on polymer surfaces (Zisman, 1964) have tempted several investigators (Owens and Wendt, 1969; Kaelble, 1970; Wu, 1973; Kloubek, 1974) to try to solve eq 3 by ignoring  $W_A^h$  and assuming that all polar and hydrogenbonding interactions can be predicted by eq 6. This forced fit of data into incorrect equations makes all conclusions at least a little wrong (e.g., finite  $\gamma^p$  values for polyethylene and paraffin).

In solution studies the separation of heats of mixing into several terms soon followed. Blanks and Prausnitz (1964) used only two terms (polar and nonpolar) while Gardon (1966) and Meyer and Wagner (1966) included terms for dipole-dipole and for dipole-induced dipole interaction. Although hydrogen bonding had been recognized much earlier (Small, 1953; Gordy, 1939), it was Hansen (1967) who brought forth the widely used three-dimensional solubility parameter

$$\Delta H_{\mathbf{M}} = \Delta H_{\mathbf{M}}^{\mathbf{d}} + \Delta H_{\mathbf{M}}^{\mathbf{p}} + \Delta H_{\mathbf{M}}^{\mathbf{h}} + \dots$$
(7)

and

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{8}$$

The dispersion force term  $(\Delta H_{\rm M}{}^{\rm d})$ , or more properly  $(\Delta U_{\rm M}{}^{\rm d})$ , can be correctly evaluated with the geometric mean

$$\Delta H_{\rm M}{}^{\rm d} \approx \Delta U_{\rm M}{}^{\rm d} = V_{\rm m}\phi_1\phi_2(\delta_1{}^{\rm d}-\delta_2{}^{\rm d})^2 \tag{9}$$

and perhaps the dipole–dipole term  $(\Delta U_{\rm M}{}^{\rm p})$  could also be estimated from

$$\Delta U_{\mathbf{M}^{\mathbf{p}}} = V_{\mathbf{m}} \phi_1 \phi_2 (\delta_1^{\mathbf{p}} - \delta_2^{\mathbf{p}})^2 \tag{10}$$

but for the reasons given in the previous paragraph there is no way that  $\Delta U_{\rm M}{}^{\rm h}$  can be predicted with a term  $(\delta_1{}^{\rm h} - \delta_2{}^{\rm h})^2$ and consequently any two sets of correlations are in serious disagreement (Bagley and Scigliano, 1975).

The extensive computer-forced correlations of heats of mixing and of works of adhesion (Kaelble, 1970; Hansen, 1967; Hoy, 1970; Hansen and Beerbower, 1971) are based on treating hydrogen bonds by the geometric mean, as if the hydrogen bond were a dipole-dipole interaction, a notion abandoned about 20 years ago (Pimentel and McClellan, 1960). A more recent approach has been developed by Drago (1971), who has treated the hydrogen bond as an acid-base interaction  $(\Delta H_M^{ab})$ 

$$-\Delta H_{\rm M}{}^{\rm ab} = C_{\rm A}C_{\rm B} + E_{\rm A}E_{\rm B} \tag{11}$$

In the referenced article Drago measured  $\Delta H_M^{ab}$  in CCl<sub>4</sub> as a neutral solvent and determined  $C_A$  and  $E_A$  for each acid and  $C_{\rm B}$  and  $E_{\rm B}$  for each base. He assumed that  $\Delta H_{\rm M}{}^{\rm d}$  and  $\Delta H_{\rm M}{}^{\rm p}$ were negligibly small for the acids and bases, and in his correlation all predicted  $\Delta H_{\rm M}{}^{\rm ab}$  values (up to 20 kcal/mol) checked measured values within  $\pm 0.3$  kcal/mol, usually within 5% or less. Drago's correlation could be corrected for differences in  $\Delta H_{\rm M}{}^{\rm d}$  by determining  $\delta^{\rm d}$  values for all components and using eq 9. Values of  $\delta^{\rm d}$  could best be determined from the ratio  $\gamma^{\rm d}/\gamma$  (determined from interfacial tensions or contact angles)

$$\delta^{d} = \delta \, \frac{\gamma^{d}}{\gamma} \tag{12}$$

However, inspection of the tables suggests that the  $\delta^d$  values for these acids and bases are about the same and only minor corrections would ensue.

Drago's correlation (treating interactions as due only to dispersion forces and acid-base interactions) is much more successful than Kaelble's and Hansen's correlations (treating interactions as due only to dispersion forces and polar interactions predictable from geometric mean equations). It is of special interest that in Drago's correlation the neglect of dipole-dipole interactions gave no problems, suggesting that dipole-dipole interactions are negligibly small compared to acid-base and dispersion force interactions.

We propose that the heat of mixing  $(\Delta H_M)$  be given by

$$\Delta H_{\rm M} = P \Delta V_{\rm M} + V_{\rm M} \phi_1 \phi_2 (\delta_{\rm A}^{\rm d} - \delta_{\rm B}^{\rm d})^2 - X_{\rm p} (C_{\rm A} C_{\rm B} + E_{\rm A} E_{\rm B}) + \Delta U_{12}^{\rm p} \quad (13)$$

where  $X_p$  is the mole fraction of acid-base pairs per mole of components present. Similarly, we propose that the work of adhesion is

$$W_{\rm A} = 2\sqrt{\gamma_{\rm A}}^{\rm d}\gamma_{\rm B}^{\rm d} - f(C_{\rm A}C_{\rm B} + E_{\rm A}E_{\rm B})$$
  
× (moles of acid-base pairs/unit area) +  $W_{\rm A}^{\rm p}$  (14)

in which the constant f (near unity) converts enthalpy per unit area into surface free energy, and the last term is usually small.

The experimental adsorption measurements of this paper are designed to test the above-stated conclusions concerning the Drago correlation, that dipole interactions are negligibly small compared to dispersion forces and acid-base interactions. In other words, in mixtures of two polar acidic compounds or two polar basic compounds we expect to find very little interaction in excess of the dispersion force interactions.

### **Experimental Details**

**Materials.** The adsorption of acidic and of basic polymers onto acidic or basic inorganic solids was determined in each of a series of solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, *p*-dioxane, and tetrahydrofuran (THF). The acidic polymer was a postchlorinated poly(vinyl chloride) (Cl-PVC), a B. F. Goodrich Hi-Temp Geon 603 × 560. Basic polymers included a duPont Lucite 4F poly(methyl methacrylate) (PMMA), with MW 5–7 × 10<sup>5</sup> and two monodisperse methyl methacrylates of MW 5.5 × 10<sup>4</sup> and 4 × 10<sup>6</sup> synthesized at Lehigh by Dr. S. Kim.

The basic solid chosen for this study was a calcium carbonate from Pfizer Minerals, Pigments, and Metals Division (Albacar 5970) with a specific surface area of 6  $m^2/g$  by our nitrogen adsorption measurements. The acidic solid was a silica powder (Aerosils 380) from Degussa Inc. with a specific surface area of 380  $m^2/g$ . For some experiments the silica was acidified by soaking overnight in 1 M aluminum sulfate and it was then filtered and dried; the surface area was then 95  $m^2/g$  by nitrogen adsorption.

**Methods.** Solutions of 0.4 to 1.5 g of polymer in 100 mL of solvent were equilibrated at 22 °C with enough filler to adsorb most of the polymer (a weight of silica about equal to the

weight of the polymer, or a weight of  $CaCO_3$  about 50 times the weight of the polymer). After about 15 min the suspension was centrifuged with a Servall SS-1 and a 10-mL aliquot of the clear supernatant liquid was evaporated to dryness, then dried for 48 h at 120–130 °C at 1–2 mm Hg pressure in a vacuum oven, and the weight of residual polymer was compared with a blank sample of the original solution. The amount of polymer adsorbed is reported in grams per meter<sup>2</sup> of filler surface. The concentration of polymer in each solvent was large enough to ensure maximum adsorption.

Desorption measurements were made with the powders centrifuged free of most of the polymer solution, oven-dried, and then redispersed in a different solvent, stirred for some time, centrifuged again, and the supernatant liquid assayed for residual polymer.

Instrinsic viscosities of the polymer solutions were determined at 20.5 °C with an Ostwald viscometer.

# **Results and Discussion**

**Solvents.** The polymers and solvents were chosen to demonstrate acidity and basicity as quantified by Drago (1971, 1976). Our neutral solvent, carbon tetrachloride, was also Drago's netural solvent. Our basic solvents (benzene, p-dioxane, and THF) and acidic solvents (CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>3</sub>) were also evaluated by Drago. The properties of the solvents are listed in Table I.

**Polymers.** The PMMA polymer is basic because of its ester groups, which are expected to be as basic as acetate groups ( $C_B$  = 3.56,  $E_B$  = 1.99). The solubility parameter is often listed at 9.3, but this may be low, for PMMA is much more soluble in THF and dioxane than in carbon tetrachloride. The post-chlorinated PVC is expected to be acidic, but not as acidic as chloroform. The solubility parameter should be somewhat greater than the 9.3 usually quoted for PVC.

Fillers. The surface acidity of silica has long been established as due to the surface silanol groups (Hair, 1967; Klier, 1973). The interaction of these acidic hydrogens with methacrylate carbonyl groups has been demonstrated by infrared spectroscopy (Fontana and Thomas, 1961), who estimated that about 40% of the ester groups were bound to the silica surface by such an acid-base interaction. The surface basicity of calcium carbonate is well established; it is the preferred filler for asphalt pavement because of its strong interaction with the acidic components of asphalt (Fowkes, 1959). The basicity resides in the carbonate ion, a moderately strong electron donor or hydrogen acceptor. The calcium ions are acidic but it is to be expected that the large carbonate anions will cover most of the surface.

Adsorption of Basic Polymer on Basic Filler. The basic PMMA polymer adsorbed to only a very slight degree onto the basic calcium carbonte filler (see Table II). A complete monolayer would correspond to about  $6 \times 10^{-4}$  g/m<sup>2</sup>, so these results indicate that only 3 to 5% of a monolayer adsorbed from benzene and carbon tetrachloride, and much less from the other solvents.

Table II

Solvent	Grams adsorbed/m <sup>2</sup> of CaCO <sub>3</sub>					
THF Dioxane C <sub>6</sub> H <sub>6</sub> CCl <sub>4</sub> CH <sub>2</sub> Cl <sub>2</sub> CHCl <sub>3</sub>	$\begin{array}{c} 0.00 \times 10^{-4} \\ 0.00 \times 10^{-4} \\ 0.2 \times 10^{-4} \\ 0.3 \times 10^{-4} \\ 0.00 \times 10^{-4} \\ 0.00 \times 10^{-4} \end{array}$					

Adsorption of Acidic Polymer on Acidic Filler. The amount of adsorption of the post-chlorinated poly(vinyl chloride) onto silica filler was less than  $10^{-6}$  g/m<sup>2</sup> (0.2% of a monolayer) for all six solvents.

Absorption of Basic Polymer on Acidic Filler. The amount of adsorption of the basic PMMA onto the acidic silica filler is illustrated in Figure 1 in which the amount absorbed is shown as a function of the acidity or basicity of the solvent. The basicity of the solvents is measured by their heat of interaction with a given acid; we have chosen *tert*-butyl alcohol from Drago's table as the acid to evaluate the basic strength of benzene, dioxane, and THF. The reason for choosing *tert*butyl alcohol is that we will be comparing the interaction of these basic solvents with the silanol groups of the silica surface, and the SiOH and ROH acids appear similar. The acidity of the acidic solvents are illustrated by their heat of interaction with ethyl acetate, an ester to be compared with the methacrylate groups of the polymer.

In Figure 1 the absorption of basic PMMA onto acidic silica is shown to be heavy from neutral solvents but to decrease with more acidic or more basic solvents. Clearly the adsorption is dominated by acid-base interactions, with an equivalent of two monolayers adsorbed from CCl<sub>4</sub>, the neutral solvent (about 50 times more adsorption onto silica than onto calcium carbonate from the same solutions).

On the right side of Figure 1 we see decreased adsorption as the acidity of the solvent increases. This illustrates the competition between the acidic solvent and the acidic silanol groups of the filler for the basic ester groups of the PMMA. Chloroform is obviously more acidic than the silanol groups for it has reduced the adsorption of PMMA to about 25% of a monolayer. On the other hand, methylene chloride allows a full monolayer of PMMA to adsorb, so it offers little competition to the silanol groups. From these findings we can estimate that the binding energy of silanol groups to methacrylate groups is about 10 kJ/mol, intermediate between the values for chloroform and methylene chloride.

On the left side of Figure 1 the adsorption of PMMA decreases as the basicity of the solvent increases. This illustrates the competition between the basic solvents and the basic PMMA for the acidic silanol groups of the silica surface. Benzene allows about one monolayer of PMMA to adsorb, so it offers no competition to the PMMA. However, dioxane allows one-fifth of a monolayer to adsorb. It appears that the

Table	I
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						$[\eta]$ , PMMA, $[\eta]$ , Cl-PVC,			
Solvent	C_A	E_A	Св	<u> </u>	€20° a	δ <sup>b</sup>	dL/g	dL/g	
THF		—	8.74	2.00	7.88	9.9	1.1	1.1	
<i>p</i> -Dioxane			4.87	2.23	2.20	10.0	1.11	0.22	
$C_6H_6$			2.86	0.22	2.284	9.15	1.20	0.36	
$CCl_4$	_		_		2.238	8.6	0.23	0.60	
$CH_2Cl_2$	0.02	3.40			9.08	9.7	1.01	0.81	
$CHCl_3$	0.306	6.77			4.81	9.3	1.69	0.79	

<sup>a</sup>  $\epsilon$  is dielectric constant. <sup>b</sup>  $\delta$  in (cal/mL)<sup>1/2</sup>; Drago constants in (kJ/mol)<sup>1/2</sup>.



**Figure 1.** Adsorption of PMMA on silica as a function of the basicity or acidity of the solvent. The basicity is shown as the heat of acid-base interaction with *tert*-butyl alcohol and the acidity is shown as the heat of acid-base interaction with ethyl acetate.

basicity of the methacrylate groups must be somewhat less than the basicity of dioxane, but much greater than the basicity of benzene. These considerations suggest that the heat of interaction of PMMA with *tert*-butyl alcohol should be less than the 12.3 kJ/mol of dioxane, but much greater than the 2.5 kJ/mol of benzene. This is confirmed by Drago's 10.5 kJ/mol for the interaction of esters with *tert*-butyl alcohol.

If sufficiently acidic or basic solvents can prevent adsorption of PMMA onto a silica filler, is this a kinetic effect or a reversible thermodynamic effect? To test this question PMMA was adsorbed onto the silica filler from  $CH_2Cl_2$ , the solvent removed, the filler dried, and then stirred in other solvents at 22 °C. We found the  $CHCl_3$  desorbed 46% of the PMMA in 20 min, and 96% in 2 weeks. Dioxane desorbed 92% in 20 min, 98% in 2 weeks. THF desorbed 92% in 20 min, and 97% in 2 weeks. These findings indicate that the solvent competition is indeed a thermodynamic phenomenon. They also suggest that chromatographic elution by a series of increasingly acidic or basic solvents could separate and identify polymers.

Figure 2 shows how a filler surface can be modified chemically to enhance acid-base interaction. The silica already discussed was soaked in aqueous aluminum sulfate overnight, filtered, and dried. Aluminum substitution in silica is known to increase the surface acidity, and Hammett acidity indicators showed increased acidity. Figure 2 compares the amounts adsorbed on the treated silica (triangles) as compared with untreated (circles). An appreciable shift to the right results, showing the treated silica can now compete for PMMA against more acidic solvents. The decreased adsorption from basic solvents was a surprise; perhaps the treated silica has smaller pores and only a fraction of the nitrogen surface (perhaps one-third) can adsorb polymer. If only 42% of the surface were available for adsorption of PMMA the results would be as shown in Figure 2 as a dashed line, indicating a very appreciable increase in adsorption from methylene chloride and chloroform.

Adsorption of Acidic Polymer on Basic Filler. Figure 3 is the same type of diagram as Figure 1, showing the amount of post-chlorinated PVC adsorbed on  $CaCO_3$  from the same solvents. The acidity of the chlorinated solvents is illustrated by comparing heats of acid-base interaction with ethyl acetate, as in Figure 1. However, the basicity of benzene, dioxane, and THF are illustrated by their heat of acid-base interaction with chloroform; this is because we wish to compare the interaction of Cl-PVC with these solvents versus the interaction



**Figure 2.** Adsorption of PMMA on silica (circles) and on silica acidified with aluminum sulfate (triangles). Dashed line compares the adsorption on acidified silica normalized for the adsorption from CCl<sub>4</sub>.



**Figure 3.** Adsorption of post-chlorinated PVC on calcium carbonate as a function of the basicity or acidity of the solvent. The basicity is shown as the heat of acid-base interaction with chloroform and the acidity is shown as the heat of acid-base interaction with ethyl acetate.

of Cl-PVC with the calcium carbonate surface, and chloroform is a better model for the acidity of Cl-PVC than is *tert*-butyl alcohol.

Again we see in Figure 3 that adsorption is strongest from neutral solvents, but diminishes even more sharply than in Figure 1 with increasing acidity or basicity of the solvents. In  $CCl_4$  or  $CH_2Cl_2$  the adsorption on calcium carbonate corresponds to about one monolayer of polymer, as compared to less than 0.3% of a monolayer adsorbed on silica from the same solutions, again demonstrating the dominance of acid-base interactions in polymer adsorption.

The left side of Figure 3 shows that all three basic solvents prevented adsorption of Cl-PVC on calcium carbonate; this must mean that the carbonate groups in the surface of calcium carbonate are weaker than benzene for acids like CHCl<sub>3</sub>.

The right side of Figure 3 illustrates the competition between acidic solvents and the acidic sites of Cl-PVC for the basic surface of CaCO<sub>3</sub>. As might be expected, chloroform is an appreciably stronger acid and so solvates the carbonate surface that no polymer can adsorb. The strong adsorption from methylene chloride means that the Cl-PVC polymer is more acidic than this solvent.

Figure 3 is important in comparing the mechanical properties of cast films of filled polymer (Marmo et al., 1976). Films of CaCO<sub>3</sub>-filled Cl-PVC were cast from CH<sub>2</sub>Cl<sub>2</sub> (in which the polymer adsorbs strongly to the filler) and from THF (in which no polymer adsorbs on the filler). The tensile strength was greater in the films cast from  $CH_2Cl_2$  and the modulus (at 40 vol % of filler) was more than double the modulus of films cast from THF. This shows that acid-base interactions at filler surfaces provide stronger composites.

# **Application to Corrosion Problems**

There are three ways in which the enhancement of adhesion by acid-base interaction of polymers with inorganic oxides can improve corrosion resistance of surface coatings: (1) Enhanced adhesion of the polymer matrix to pigment particles can ensure complete coating and separation of particles, thereby eliminating particle-to-particle pathways for diffusion of corrosive media or of electric current carriers through the paint or enamel. (2) Enhanced adhesion of polymer coatings to the oxide surface of metals (many of which oxides are strongly acidic or basic) can minimize access of corrosive media to the metal surface through lifting or blistering of paint from the metal oxide at holes, scratches, or edges. (3) Metal oxide surfaces can be modified chemically to enhance acidbase interaction with surface coatings, and by exploiting strong "soft" acid-base interactions can minimize susceptibility of coated metals to aqueous media.

#### Conclusions

1. The adsorption of polymers onto fillers from organic solvents is dominated by acid-base interactions of the solvent, polymer and filler surface.

2. Negligible adsorption occurs unless there is an acid-base interaction between the polymer and filler surface. Dipole interactions between polymer molecules having many local dipoles and filler surfaces with dipolar sites were negligibly small compared to acid-base and dispersion force interactions.

3. Acidic or basic solvents tend to compete for the polymer or the filler and if the solvents are acidic or basic enough, no adsorption will occur.

4. Such competition of acidic or basic solvents with poly-

mers or fillers is a means of measuring the acidity or basicity of both polymers and fillers.

5. The surface of fillers can be chemically modified to enhance acid-base interaction and increase adsorption.

6. The surface silanol groups of silica are not quite as acidic as chloroform, as judged by the interactions of PMMA. The surface of calcium carbonate is basic, but even less basic than benzene, as judged by the interactions of chlorinated PVC.

7. PMMA is much more basic than benzene, and nearly as basic as dioxane or THF, as judged by interactions with SiO<sub>2</sub>. This is in perfect agreement with Drago's measured enthalpies of interaction. Chlorinated PVC is much more acidic than methylene chloride but not as acidic as chloroform, as judged by the interactions with calcium carbonate.

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