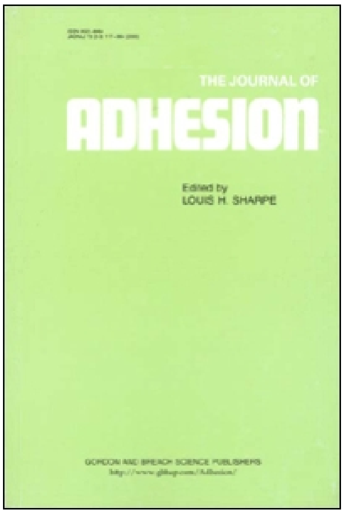

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Component Interaction and Properties of Pigmented Epoxy Systems†

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Acid-base interaction parameters have been measured for components of epoxy resins, including various pigmenting solids, using the method of inverse gas chromatography. The influence of acid-base interactions was then evaluated in terms of cure rates and the performance of the epoxy formulations as adhesives in metal joints. It has been found that non-polar particulates do not affect cure rates significantly; strongly acidic and basic pigments such as an iron oxide and a rutile, both retard the reaction, while a mildly basic $CaCO_3$ filler tended to accelerate the curing process. The initial bond strength of joints using the epoxy as sealant also varied with the choice of particulate, as did bond strength retention following exposure to selected temperature-humidity cycles. The effects exerted by the particulates are postulated as being due to selective sorption mechanisms. It is believed that the strongly basic rutile immobilizes the mildly acidic epoxy molecule, while the strongly acid iron oxide tends to immobilize basic catalyst and accelerator molecules. Both tend to slow reaction rates, but only the immobilization of epoxy by a basic particulate surface also produces benefits in bond strength and bond durability.

KEY WORDS Acid-base interaction; adhesive properties; component interaction; epoxy systems; fillers; peel strength.

INTRODUCTION

In recent years considerable attention has been given in our laboratory to the measurement of interactions among the com-

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ponents in multi-phase polymers, and to the effects of interactions on polymer properties. As to measuring interactions among the components, the inverse gas chromatography (IGC) method[1,2] has been adapted for the purpose. By standardizing on vapors known to be Lewis acids and bases,[3] it is possible to define an interaction potential parameter, Ω, which ranks polymeric and other non-volatile stationary phases in the IGC experiment as to their donor-acceptor tendencies.[3] This technique has been used with thermoplastic polymers, their blends and composites, in order to clarify the importance of interaction balances on mechanical and rheological properties, among others.[4,5]

A logical extension to the cited work involves thermosetting, crosslinked polymers. In the present instance epoxy systems have been chosen as representative of this polymer category. Specifically, we report on the influence of pigments on crosslinking phenomena and on the adhesion of joints with the epoxy as sealant. The use of pigments and other particulates in epoxy formulations is, of course, well known.[6] Such materials as mica, $CaCO_3$, talc, inorganic and organic colorants are present frequently to modify a host of characteristics, ranging from moisture sensitivity and thermal expansion coefficients to the amount of heat liberated during hardening reactions.[6,7,8] In this work, particulates have been chosen from the pigment group as well as from the range of solids usually added to reduce cost or to control specific properties of the composite. Attempts are made to rationalize modifications in crosslinking and adhesion characteristics brought on by the additives in terms of the specific interactions represented by Ω values. We intend thereby further to evolve an understanding of behavior patterns in multi-component polymer systems.

EXPERIMENTAL SECTION

i) Materials

The epoxy resin used in this work was Epon R-2004, a commercial product supplied by Shell Canada Ltd. Its fusion point was found to be 70°C. Two crosslinking agents were used. One was Epon P-100, an imidazole compound produced by Shell, with a fusion temperature of 64°C. The second, also from Shell, was Epon P-108, a dicyandiamide containing imidazole as accelerator, with a fusion point at 203°C.

The following were the particulates involved in the study:

- TiO_2-rutile; a commercial surface treated pigment with an average particle size of 0.2 μm and a BET surface area of 8.9 m^2/g.
- Fe_2O_3-ferric oxide; a commercial specimen with average particle size of 0.8 μm.
- Mica-phlogopite mineralization; a platelet solid screened to provide fraction in the $-40+70$ size range.
- $CaCO_3$; a commercial, surface-treated sample, B.E.T. surface area 5.5 m^2/g, and average particle size of 1.2 μm.

ii) Procedures

Compounding All Epons were dried under vacuum for 24 h prior to use, and all particulates were heated to 150°C under vacuum prior to compounding. To prepare test compounds, materials were tumble-blended for 30 min on a roll mill, then re-ground in a Wiley mill and tumble-blended again (1 h) to ensure uniform distribution. The composition of specimens was as follows:

I. Epon R-2004 . . . 100 parts
Epon P-100 . . . 5 parts
Particulate . . . 10 parts

II. As above, but Epon P-108 replacing P-100.

Interaction characteristics Columns for IGC experiments were prepared by mixing one part of each of the solids individually with ten parts inert glass beads (0.5 mm radius). In all cases the solids content was between 3–5 g; a column containing glass beads was used to provide a correction to the retention data generated in columns containing the active agents in our compounds. The details of IGC experiments were described previously;[4,5] *n*-octane, *t*-butanol and butylamine were neutral, acid and base vapor probes respectively. At least triplicate elution trace determinations were used to evaluate retention times and specific retention volumes (Vg°), following the conventions described in Reference 4. Interaction parameters Ω were calculated for acidic solids (Vg butanol < Vg° butylamine) from

$$\Omega = 1 - (Vg^{\circ})_{\text{amine}}/(Vg^{\circ})_{\text{alcohol}} < 0 \quad (1)$$

and for basic solids (Vg° butanol > Vg° butylamine) from

$$\Omega = (Vg^{\circ})_{\text{alcohol}}/(Vg^{\circ})_{\text{amine}} - 1 > 0 \quad (2)$$

The parameters were obtained from 30–120°C, with a repeatability better than 5%. Though it would be desirable to extend the Ω data over the entire temperature range of crosslinking reactions, the sharp decrease in Vg° at higher temperatures made this impractical.

Reaction processes A Perkin–Elmer DSC-2 differential scanning calorimeter was employed to measure reaction exotherms in the range 50°–280°C at linear heating rates of 5, 10 and 20°C/min. Isothermal determinations of reaction heats were also conducted at selected points within that temperature range. The degree of conversion (α) from initial to final products was evaluated following Barton,[9] using ratios of reaction exotherms at any time t and at equilibrium,

$$(\alpha) = \Delta H_t / \Delta H_{\infty} \quad (3)$$

Whenever possible, isothermal experiments were also used to determine the induction times, t_1, for the onset of exothermic reactions. This was done to show the degree to which component interactions may accelerate or attenuate crosslinking reactions in the chosen epoxy formulations.

Adhesion performance Adhesive joints were prepared for peel strength testing, according to ASTM D903-49.[10] Samples were prepared by applying a 300 mg sample of epoxy formulation to a 20 cm × 2 cm test panel sheet (Bonderite-1000 Cold-Rolled steel) and covering this with alumnium foil cut to 40 cm × 2.5 cm dimension. All metallic parts of the joint were previously cleansed in trichloroethylene vapor under reflux, then washed in distilled water and dried at 150°C under N_2. The assembled parts were then exposed to 70°C at 10,000 lb/in^2 (743 kg/cm^2) for 1 min to form a cohering "sandwich". These structures were then cured at a temperature in the range 120–170°C for 10 mins.

Peel testing was done on six samples of each formulation, using an Instron table model tester. This pulled the flexible aluminium foil from the assembly at a 180° angle and a separation speed of 10 cm/min.

Adhesive properties were measured on samples as prepared (initial properties) and after specimens had been subjected to accelerated aging routines (residual properties). In one cycle of this routine, the specimen is conditioned for 24 h at ambient conditions, then is placed in a chamber at 60°C and 80% R.H. for 24 h, then in a dry compartment (24 h) at −55°C, before being returned to ambient conditions for a final 24 h. Up to 20 cycles were applied to certain samples, and peel test evaluations were performed after selected numbers of cycles.

RESULTS AND DISCUSSION

i) Interaction Characteristics

Values of Vg° and Ω for the particulates and the epoxy components are given in Table I. Also indicated in the Table are the ratios of Vg° values at the extreme temperatures—*i.e.* $(Vg^\circ)_{120^\circ}/(Vg^\circ)_{30^\circ}$ so as to show the extent of temperature variations in the retention characteristics.

As might be expected from their chemical structures,[11] the epoxy and the two crosslinking agents are respectively acid and base. Of the two crosslinkers, Epon P-100 is the stronger base, its Ω value attaining values >1.0 at temperatures above 60°–70°C. Among the particulates, the rutile represents a strong base, the surface of Fe_2O_3 is a relatively strong acid and $CaCO_3$ is a weak base. The mica has Ω values sufficiently close to zero to be considered, in essence, as a solid surface in which dispersive forces dominate over polar forces. The evident temperature dependence of Ω is due, presumably, to the differences in bonding energies between solid-vapor pairs exhibiting acid-base coupling and those in which van der Waals forces dominate, or where polar force repulsion can be envisaged. The ratios of Vg° at 120° and 30° provide a rough guideline in this regard. Assuming octane to be a non-polarizable molecule, it is evident that regardless of which solid is being contacted, dispersion-force bonds generate a ratio of about 0.3. In

TABLE I
IGC parameters for epoxy and particulate components

Material		(Vg°): nC_8		*n* but. amine		*t*. butanol		Ω
Epon R2004: @ °C	30	27.6	0.36	35.2	0.53	28.7	0.40	−0.23
	60	20.3		30.3		23.0		−0·32
	90	14.3		24.0		17.3		−0.39
	120	9.9		18.5		11.6		−0.59
Epon P-100: @ °C	30	20.4	0.33	19.5	0.31	29.4	0.62	0.51
	60	15.1		14.8		24.4		0.65
	90	10.3		9.3		20.9		1.25
	120	6.7		6.1		18.3		2.00
Epon P-108 @ °C	30	33.7	0.35	31.5	0.37	41.0	0.51	0.30
	60	25.6		25.8		32.7		0.27
	90	19.1		19.1		26.9		0.41
	120	11.7		11.5		20.8		0.81
Mica @ °C	30	40.5	0.30	26.8	0.30	27.7	0.36	0.03
	60	31.3		19.5		21.6		0.11
	90	19.4		10.8		11.3		0.05
	120	12.0		7.9		10.0		0.27
TiO_2: @ °C	30	167	0.32	132	0.43	299	0.63	1.26
	60	113		106		274		1.58
	90	75.2		80.1		230		1.87
	120	53.9		57.2		288		2.29
Fe_2O_3: @ °C	30	116	0.32	128	0.55	89.8	0.44	−0.43
	60	81.9		106		73.6		−0.44
	90	55.3		93.2		60.4		−0.54
	120	37.4		70.7		40.0		−0.77
$CaCO_3$: @ °C	30	27.0	0.36	22.8	0.38	30.9	0.43	0.35
	60	20.1		17.4		23.1		0.33
	90	16.6		13.5		18.1		0.34
	120	9.7		8.8		13.4		0.51

the pairs where strong acid-base coupling appears to occur—namely TiO_2-butanol and P-100-butanol, the Vg° ratio is near or above 0.6, while for moderate bonding the ratio value may be expected to lie in the range 0.4–0.5. If these guidelines truly reflect the interaction phenomena at interfaces, then with a substrate such as mica, the presence of polar hydroxyl and amino groups in the vapor probe contributes little to the bond strength. Similarly in cases such as P100-butyl amine, $CaCO_3$-butyl amine, and possibly R2004-butanol, the vapor molecules appear to be so oriented at the solid surface as to interact with it through (predominantly) dispersion forces.

ii) Reaction Processes

Two parameters have been chosen to illustrate the crosslinking processes taking place in the defined epoxy formulations. As already indicated, these are the degree of conversion, α, of epoxy to crosslinked resin, obtained from reaction isotherms,[9] and the induction time, t_1, for the onset of reaction. Additional parameters, including total exothermic heats of reaction will be reported in a subsequent publication. A number of the reaction isotherms for reference compositions, without particulate additives, are shown in Figure 1. These differentiate strongly between the crosslink effectiveness of the two agents; P-108, containing imidazole accelerator, triggers significant reaction at temperatures above about 100°C, while no significant signs of reaction could be detected by present methods below 120°C when P-100 was involved. At the upper end of the temperature scale, above ~180°C reaction rates were too rapid to be analyzed meaningfully with P-108 reagent, but could be followed to ~220°C with P-100. The presence of the accelerator, clearly exerts a strong influence on the reaction processes.

Referring to Table I, and assuming that trends in the temperature variations of Ω are maintained beyond 120°C, stronger acid-base coupling would be expected in the Epoxy-P-100 system than in the

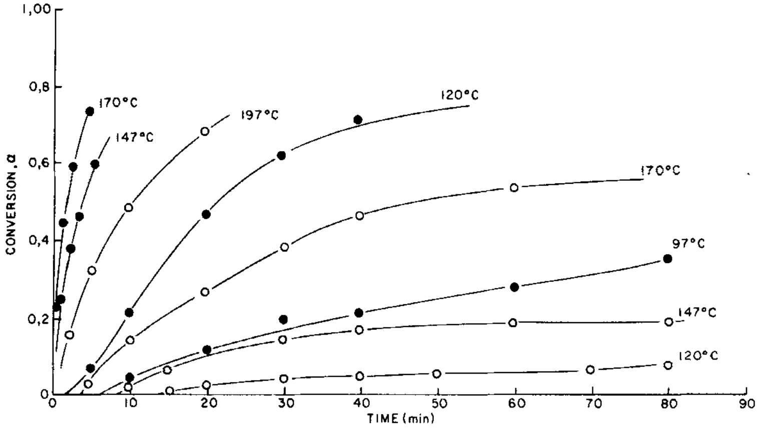

FIGURE 1 Rates of epoxy conversion as function of temperature and catalyst choice.

○ P-100 catalyst ● P-108 catalyst

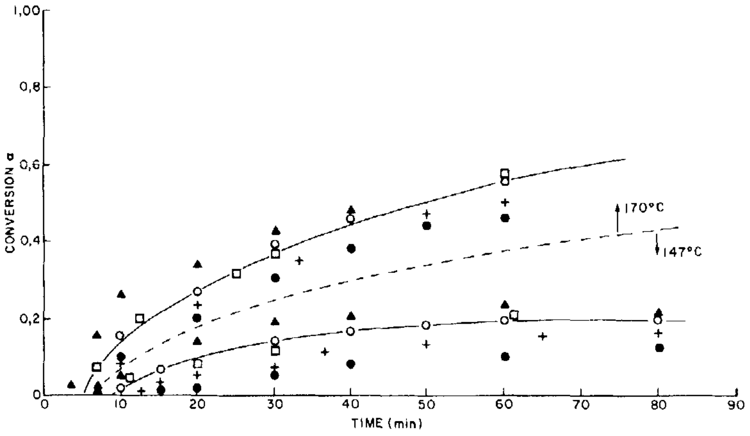

FIGURE 2 Influence of particulates on isothermal epoxy cure processes: System epoxy/P-100.

○ No filler ▲ $CaCO_3$ + TiO_2
□ Mica ● Fe_2O_3

corresponding P-108 system. Apparently this is not an important factor in the determination of reaction rates in the unpigmented compounds.

The effect of particulates on reaction proceses, however, does appear to depend on specific interactions among the components. An illustration is given in Figure 2, showing the response of the system epoxy-P-100 to the presence of the particulates. Isotherms at 147°C and 170°C have been chosen for the illustration which typifies the trends at other reaction temperatures, and also serves as an example of similar trends noted in the epoxy-P-108 system. As shown in Figure 2, mica has virtually no modifying effect on the crosslinking process. The $CaCO_3$ acts as a mild accelerator, the influence being particularly noted in the initial stages of reaction. In contrast, both TiO_2 and Fe_2O_3 reduce the rate of conversion and seem to produce final products with lower degrees of conversion and thus, lower crosslink densities.

An analogous effect is noted in t_1. The temperature dependence of this parameter is shown for epoxy-P-100 in Figure 3, and for epoxy-P-108 in Figure 4. The choice of abscissa was dictated by the empirical observation that such a representation produced very satisfactory linear functions. The effects in these cases are internally

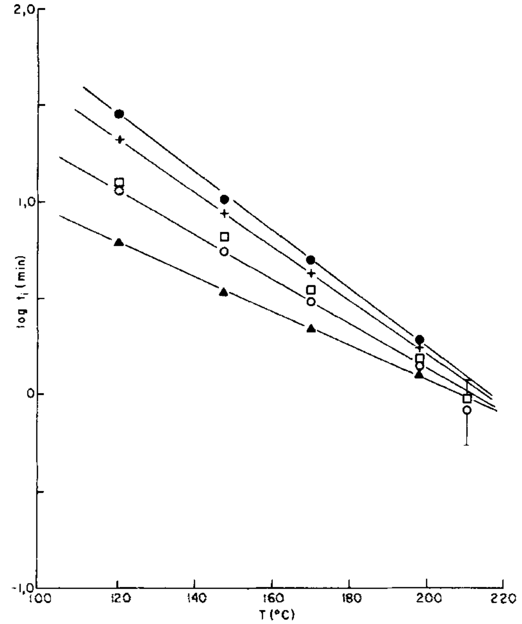

FIGURE 3 Induction time vs. temperature for epoxy cure reaction: System epoxy-P-100.

○ No filler ▲ $CaCO_3$ + TiO_2
□ Mica ● Fe_2O_3

consistent. A decrease in the induction time is produced by the $CaCO_3$, while TiO_2 and Fe_2O_3 attenuate the onset of reaction appreciably. Again, in neither case does mica influence the induction time for reaction.

Qualitatively, these observations may be rationalized in terms of apparent acid-base interactions, and selective sorption phenomena which arise as a result. In this scheme mica reflects its weakly interacting surface, and does not sorb effectively any of the chemical reactants. The present rutile and iron oxide samples, with Ω ratings in the strong basic and acidic group, may be assumed to sorb their counterparts selectively, as demonstrated by analogous work reported by Fowkes and coworkers.[12] Accordingly, rutile will tend to immobilize the epoxy molecule, while the basic imidazole and dicyandiamide molecules will tend to be immobilized by the acidic iron oxide pigment. The (partial) immobilization either of

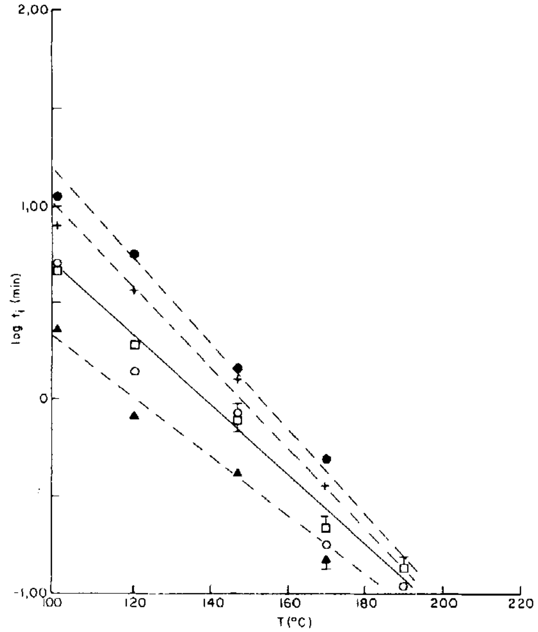

FIGURE 4 As in Figure 3: System Epoxy-P-108.

epoxy or crosslinking chemical reduces the reaction rate and increases the induction time for reaction. Of the two, the sorption of crosslinking agent appears to be the more effective route to slowing the thermosetting reaction, since relatively larger effects are noted due to the presence of Fe_2O_3 than to that of the present rutile specimen. The most interesting, and complex case, is that of $CaCO_3$. This mildly basic surface accelerates reaction parameters; for consistency, therefore, there cannot be effective immobilization of the epoxy molecule in this instance. The question of effective immobilization then would depend on the difference in the Ω values for interacting species. At present, no guidelines can be offered from theoretical considerations as to what represents a minimum $\Delta\Omega$ for strong interaction. Empirically, using 120°C as a representative reaction temperature, it follows from Table I that $\Delta\Omega \geq 1.5$ produces partial immobilization leading to an attenuation of reactions. The $\Delta\Omega$ for epoxy-$CaCO_3$, near 1.0, may be sufficient to reduce the free mobility of the epoxy without, however, inhibiting its chemical reactivity. Thereby the crosslinking process is accelerated. Some further discussion of this interpretation follows below. Clearly, however, additional experiments will be needed to test the validity of the concept.

iii) Adhesion Performance

Initial bond strengths of control and filled epoxy formulations, determined by peel testing as outlined above, are reported in Table II. The data—at 120° and at 170°C—represent the full temperature range for cure, and are typical of all results obtained. Two features are immediately evident: Firstly, the choice of catalyst significantly affects the initial bond properties; secondly, the presence of particulates may alter these bond properties in either direction. Increases in peel strength, 40–60% in magnitude, may be realized by using the dicyandiamide/imidazole catalyst (P-108) in place of the imidazole compound (P-100) alone. The differences, observed both in control and filled compounds, suggest that different network morphologies, and perhaps different surface energetics, are produced by these catalysts. Evidence supporting the generation of distinctive network morphologies by these catalyst classes has been reported by Cagle.[13]

The ability of particulates to affect bond performance is not dependent on the catalyst involved but appears to vary significantly with the interaction potential of the filler. Mica, which did not affect crosslinking processes, again fails to exert significant influence. The initial bond properties, when mica is present, are within the

TABLE II
Initial adhesive bond strength for variously filled epoxy systems

	Adhesive Bond Strength (kg cm^{-1})			
Catalyst Cure condition:	P-100		P-108	
(°C/min)	120°/10	170°10	120°/10	170°/10
Additive:				
None-control	0.58	1.12	0.95	1.62
TiO_2	0.86	2.07	1.63	2.86
Fe_2O_3	0.53	0.97	0.84	1.40
$CaCO_3$	0.64	1.22	1.09	1.91
Mica	0.59	1.07	0.91	1.55

experimental error of control structures. Rutile and $CaCO_3$ increase peel strength, the former predominantly by 60–80%, the latter by some 10–20%. As suggested by the relevant acid-base parameter (Ω) values, the rutile should interact with or sorb the epoxy strongly, while weaker interaction would be expected between epoxy and $CaCO_3$. The iron oxide, which would be expected to interact with the basic catalysts, decreases initial bond characteristics, typically by some 10–15%.

The contribution of fillers to bond properties is even more evident in samples which had been aged by the temperature-humidity cycles described earlier in this article. Figures 5 and 6 document the point, the former showing percent changes in bond properties for epoxy-P-100 systems, the latter for corresponding epoxy-P-108 formulations. The most obvious contrast is between the ability of TiO_2 to stabilize and of Fe_2O_3 to destabilize bond properties. $CaCO_3$ retains a mild stabilizing tendency, while mica again appears not to be involved in the interfacial characteristics of these structures. Qualitatively, these findings are consistent with the

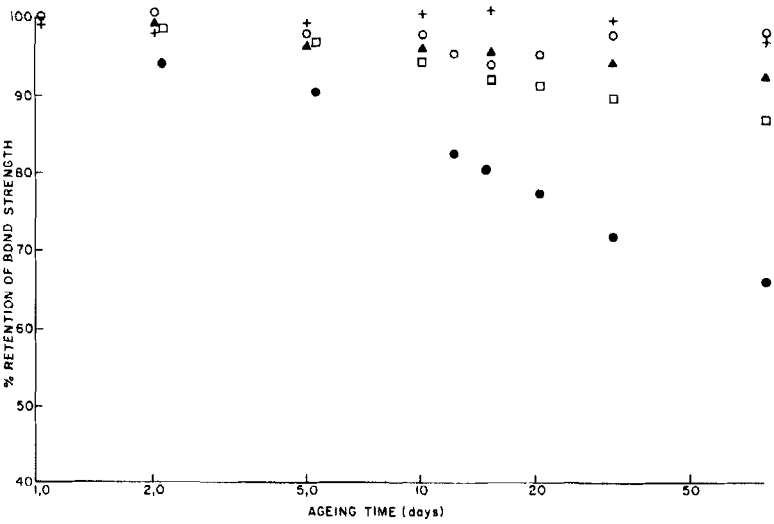

FIGURE 5 Retention of bond strength in joints using pigmented epoxy/P-100 system as adhesives. Cure conditions 170°C/10 min.

○ No additive ▲ $CaCO_3$ + TiO_2
□ Mica ● Fe_2O_3

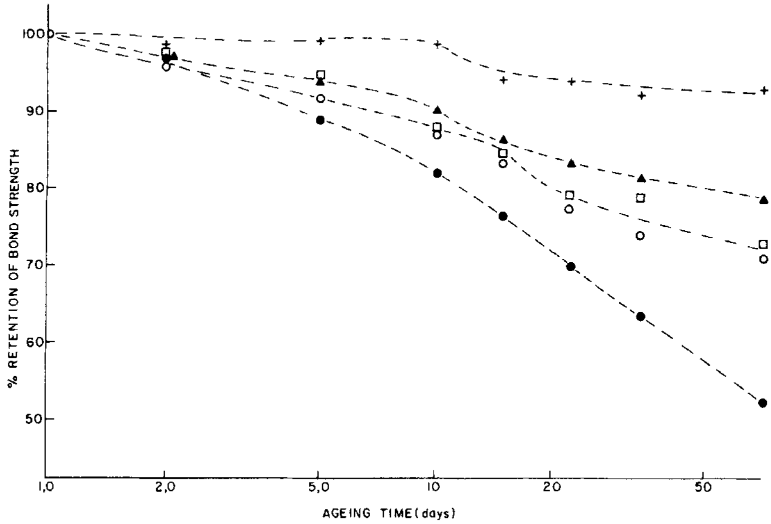

FIGURE 6 As in Figure 5: System epoxy/P-108 as adhesive.

suggestion that fillers sorbing the epoxy molecule become integral parts of the crosslink structure in the cured resin, while the inherent incompatibility between the epoxy and acidic particulates, such as the present iron oxide,† produce a crosslink structure with imperfections or microvoids in the region of the particulates. This would account for the differences in initial bond strengths; furthermore, since imperfections in the particulate/matrix interphase would act as routes for the intrusion of water, for the concentration of mechanical strains, etc., more rapid deterioration of bond and mechanical properties would be expected.

The final point to be considered here is the origin in acid-base interaction tendencies of the time-dependent changes in bond properties. Following the notions introduced above, the percent changes in bond strength were plotted against the Ω values of particulates. Figure 7 illustrates the result, using the data after 60 days of aging cycles. Entirely analogous results are obtained at other aging times, showing that the increasing stability in bond

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† Since most commercial particulates have been surface treated, we stress that present remarks pertain to the specific specimens examined and do not necessarily apply to other versions of the particulates.

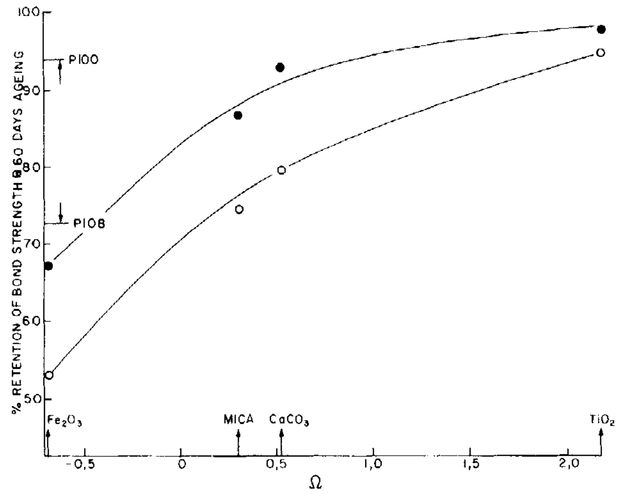

FIGURE 7 Apparent relationship between bond strength retention and acid-base interaction among components in epoxy formulations.

○ P-108 catalyst ● P-100 catalyst

strength and increasing basicity of the particulate are directly linked. Thus, for the acidic epoxy used here, the acid-base interaction concept seems to provide a useful guideline both to the initial bond properties and to their time-dependent variations in aggressive environments. Further work is planned to clarify the many implications of these findings.

Acknowledgment

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