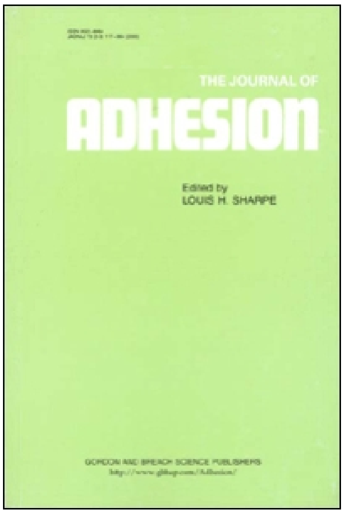

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Bond Characteristics at Pigment-Polymer Interfaces*

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An assessment was made of the effectiveness of bonding polymers from solution to dispersed solids by dispersive and non-dispersive forces. The polymers included neutral low density polyethylene (LDPE), a basic ethylene co-vinyl acetate (EVA) and an acidic chlorinated polyethylene (CPE). The solids included surface coated rutiles, an organic colorant and the chromatographic support Chromosorb.® The quality of polymer-solids bonds was estimated by eluting adsorbed polymers with *p*-xylene under reflux. The amount of polymer recovered was a function of acid-base forces acting at the polymer-solid interface. LDPE was recovered quantitatively, as were EVA and CPE when these were adsorbed on like (acid or base) solids but recovery was limited when significant acid-base interaction occurred. These results were relevant to the stabilization of solids dispersed in polymer solutions. Sedimentation experiments noted that the absence of acid-base interactions as well as an excess of these non-dispersive forces was detrimental to the stability of dispersions. For the specific systems under study, however, it was possible to define a preferred, intermediate range of acid-base interactions for dispersion stability. The configuration of adsorbed polymer chains was suggested to be an important consideration in this regard.

KEY WORDS: polymer adsorption; adsorption isotherms; acid-base forces; dispersion stability; configuration of adsorbed polymer; elution; polymer-solids bonds; adhesion

1 INTRODUCTION

Interfaces in multi-component polymer systems merit the broadening scope of investigation directed at understanding them, given their profound influence on processing and use properties of the polymers. The research group headed by Jacques Schultz, to whom this paper is dedicated, has done seminal work to clarify the issue. Notable among the many advances made to understanding the behavior of polymers at interfaces are Schultz's contributions to phenomena of polymer restructuring[1,2] and his use of chromatographic techniques to underline the importance to adhesion of acid-base interactions.[3] These items are relevant to this presentation.

The present inquiry is directed at interfaces in dispersions of solids in polymer solutions. Understanding the properties of such dispersions is important to technolo-

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* One of a Collection of papers honoring Jaçques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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gies in areas as diverse as protective coatings and xerography.[4] In a preceding report on related work,[5] it was shown that the adsorption of polymers on rutile (TiO_2) pigments was strongly influenced by the existence of specific, acid-base interactions between the adsorbing polymer and the solid substrate. This confirmed earlier findings along similar lines by Fowkes.[6] The stability of pigment dispersions in polymer solutions must depend on the adsorbed state of the macromolecule, and the inference to be drawn from the earlier studies, therefore, indicates that the nature of acid-base interactions may once again be of concern. The question is pondered through the use of acid-base descriptors for polymers and pigmenting solids, as determined by the techniques of inverse gas chromatography (IGC)[3,7,8] and, in specified cases, through estimates of the strength of acid-base forces.

2 EXPERIMENTAL

2.1 Materials

Three polymer solutes were used in this work. They were selected on the basis of their specific interaction potential. A low density polyethylene (LDPE) represented the neutral category, a chlorinated polyethylene (CPE) was the acidic polymer, while an ethylene-co-vinyl acetate (EVA) was the basic polymer representative. The LDPE was a melt index 4.0 resin obtained from Novacor Inc. CPE was a product of DuPont Canada Inc. and the EVA, with a VA content of 28 mole-%, was from AT Plastics Inc. In procedures using polymer solutions, the solvent was reagent grade trichlorobenzene (TCB).

The dispersed solids of this work included three samples of rutile, TiO_2, each with different surface coating. A Monastral Green was used as a representative of organic pigments. These materials were supplied by Tioxide Canada, Inc. Chromosorb® A/W 60/80 mesh, a conventional chromatographic support from Chromatographic Specialities (Canada) Ltd., was also used as a dispersed phase. The surface areas of the solids were determined from B.E.T. adsorption isotherms for nitrogen at $-196°C$.

2.2 Experimental Procedures

2.2.1 Surface interaction potentials The IGC procedures already noted[3,7,8] were used to determine the dispersive contribution to the surface energy of polymers and particulates, (γ_s^d). For the purpose, the polymers, supported on Chromosorb and particulates were the stationary phases in experiments with the *n*-alkane series from hexane to decane used as vapor probes. A Varian Model 3400 gas chromatograph, with flame ionization detectors, was the apparatus. The temperature of determination throughout scanned the range from 30° to 60°C, helium was the carrier gas and methane was used as marker. The closely monitored flow rate of carrier gas was 20 mL/min. Symmetric elution peaks were obtained for triplicate injections of vapors, and from these were calculated retention times and volumes, with an uncertainty of $\pm 3\%$. Following the discussion in Ref. 8, values of γ_s^d were obtained from the slopes of diagrams in which $RT \ln V_g$ was plotted against T_b, where V_g is the specific retention volume and T_b the normal boiling temperature of the vapor probes. The acid-base concepts of Gutmann[9] led to the choice of benzene and chloroform as the acidic vapors, and of diethyl ether and tetrahydrofuran as the basic vapors with which to determine the acid-base interaction potential of the solids used in this research. The position of retention volumes for these probes, relative to the V_g of an alkane of the same boiling point, defined ΔG^{ab}, the acid-base contribution to the free energy of adsorption of the vapors. That value was used to determine the acid-base interaction constants Ka and Kd for the solids, following the procedures of Papirer[7] and Schultz.[3] Ka and Kd, respectively the acid and base interaction potentials of each solid, were then used to calculate a pair interaction potential, Isp, for polymer/particulate combination from,

$$\mathrm{Isp} = (\mathrm{Ka})_1 \cdot (\mathrm{Kd})_2 + (\mathrm{Ka})_2 \cdot (\mathrm{Kd})_1 \tag{1}$$

2.2.2 Adsorption of polymers and the polymer/particulate bond The capacity of the various particulate surfaces for the adsorption of polymers was obtained from adsorption isotherms, following the procedure described earlier.[5] Briefly, accurately weighed amounts of particulate were contacted with 20 mL of polymer solution at 120°C and at a constant polymer concentration of 1.00 wt.%. The dispersions were agitated for about 6 h, whereupon solids were deposited by centrifugation and aliquots of the clear supernatant solutions were analysed for residual dissolved polymer. This was done by removing the TCB solvent under vacuum at 95°C until invariant quantities of polymer remained. Generally, the procedure required up to 48 h of evacuation and led to estimates of adsorbed polymer precise to ±8%.

In order to estimate the strength of bonds at the polymer/particulate interface, solvent extraction experiments were performed on solids with known quantities of adsorbed polymer. The previously determined adsorption isotherms served as guidelines in this aspect of the work, the quantities of polymer retained by the solid being given by the maximum, or plateau adsorption capacity for each polymer/solid combination (see section 3.2 of this paper for greater detail). Weighed amounts of carefully dried solids were placed in a Soxhlet extraction apparatus, and eluted under reflux with excess, distilled *p*-xylene for up to 7 h. Periodically, aliquots of solution were removed and evaporated to invariant weight of dissolved polymer by a procedure similar to that described above, thereby providing a measure of the rate of polymer removal from the particulate surface.

2.2.3 Stability of solids dispersions Dispersions of each polymer/solids combination were made by placing in a glass jar 10 wt.% of particulate in 60 mL of 0.5 wt% polymer solution. To this was added 300 g of 0.4 cm diameter stainless steel balls, acting as a grinding medium. The stoppered jar tumbled for 48 h on a two-roll mill operating at 20 rpm. The disperions were then decanted from the grinding medium, and samples placed in previously calibrated, graduated 10 mL centrifuge tubes. The tubes were placed in a vibration-free space and the volume of clarified supernatant solution was recorded for periods of up to 7 days. Finally, the systems were centrifuged and the volume of sedimented solids was recorded.

3 RESULTS AND DISCUSSION

3.1 Material Characteristics

The surface and interaction properties of the materials used here are recorded in Table I. The dispersive surface energies show relatively little variation among the various substances. The values for rutile are strongly affected by the surface coatings applied to them, since an uncoated rutile (not used in this research) had a γ_s^d of about 62 mJ/m^2. The three polymers have only slightly different dispersive surface energies but, of course, the presence of VA and Cl groups in EVA and CPE, respectively, elevates the total surface energies of these polymers above that of LDPE. The acid-base characteristics of the materials differ appreciably. The choice of polymers is justified by the interaction parameters: As expected, the LDPE has neither electron donor nor acceptor capability, so that the adsorption of this polymer on solids can be stabilized by dispersive Lifschitz-van der Waals (L/W) forces only. The Ka, Kd values for EVA and CPE identify these as prevalently base and acid, respectively. In the light of the corresponding parameter values for the particulates, significant acid-base contributions to the bonding of polymer adsorbates may be expected in combinations such as EVA/R-2 and CPE/R-3. The amphoteric rutile R-1 may provide a surface which is generally suitable for the adsorption (retention) of either acidic or basic polymer groups. The Monastral Green surface is considered to be very weakly acidic, that of Chromosorb amphoteric, but close to neutrality. L/W forces may predominate in the adsorption of polymers on these solids.

3.2 Adsorption of Polymers and the Nature of Adsorption Bonds

The adsorption isotherms, illustrated in Figure 1 by three polymer/solids combinations, were invariably of the Langmuir type, with well-defined plateaus, or maximum values of adsorbate. In this, they resembled the shape of isotherms reported earlier[5] for several polyester/pigment systems. The abscissa and ordinate variables in Figure 1 are expressed in terms which eliminate the dependence of isotherms on the quantity of particulate used in the experiment.[10] The plateau values, obtained by graphical extrapolation as indicated in the figure, differ among the combinations, for example

TABLE I
Characterization of Experimental Materials

Material:	Surf. Area (M^2/g)	$(\gamma_s)^d$ (mJ/M^2)	Ka	Kd
Rutile R-1	9.0	45.5	3.1	3.9
Rutile R-2	8.6	44.2	5.2	1.8
Rutile R-3	10.3	50.1	3.0	5.7
Mon. Green	55	42.6	1.6	0
Chromosorb®	1.1	32.5	0.9	0.3
LDPE	–	31.0	0	0
EVA	–	33.6	1.7	4.4
CPE	–	32.8	5.0	2.3

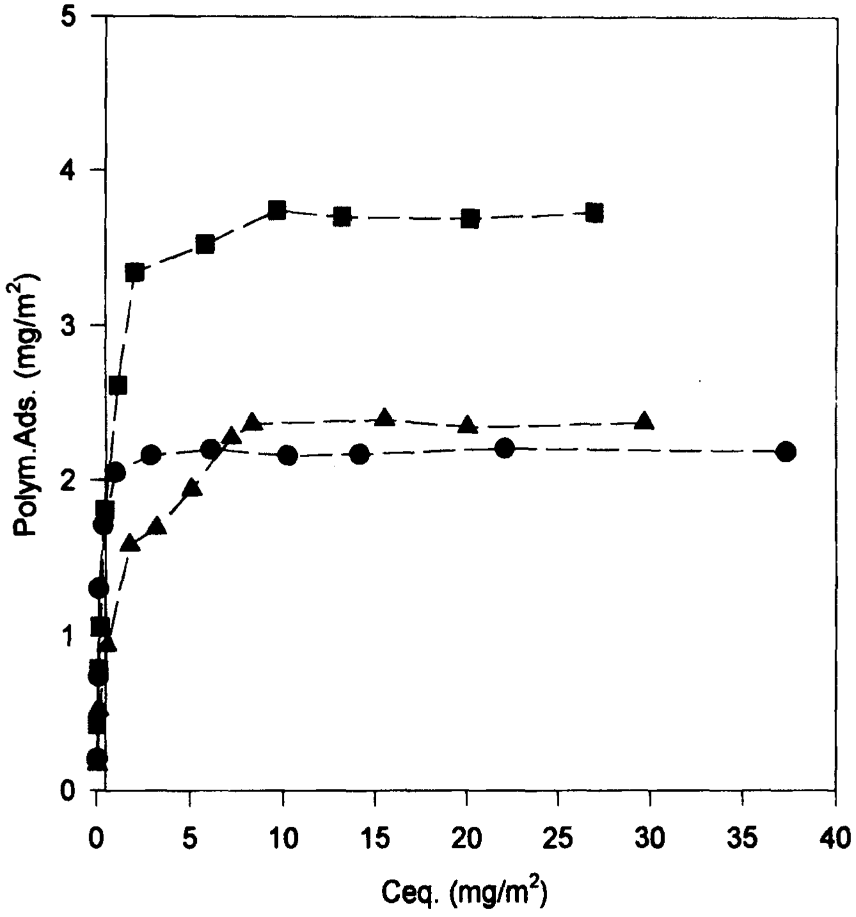

FIGURE 1 Typical adsorption isotherms (120°C) for polymers on solids. ● LDPE on rutile R-2; ▲ LDPE on Monastral Green; ■ CPE on rutile R-3.

CPE/R-3 showing a much greater adsorption capacity than the isotherms for LDPE adsorbate. Implied is the influence of acid-base forces, already alluded to above.

The data summary of Table II confirms the point. The link between the magnitude of acid-base forces and plateau adsorption values is evident in the behavior of EVA and CPE adsorbates. The highest plateau datum for EVA occurs with R-2, the combination also with the highest Isp value. The pairing CPE/R-3, as anticipated earlier, reports both the highest plateau and Isp data for that polymer. Further in line with earlier statements, the amphoteric R-1 adsorbs both EVA and CPE to a significant extent. The neutral adsorbate, LDPE, has nearly identical plateau values on all solids except Chromosorb. The surface free energies of the solids, with the exception of Chromosorb, are significantly greater than that of LDPE. The drive for polymer wetting the surfaces, therefore, is weakest with Chromosorb. Thus, at the elevated temperature of the isotherm, the tendency for polymer adsorption also is limited.

Interestingly, the polar polymers do not adsorb massively on either the organic pigment or on Chromosorb. In the latter case, weak surface free energy drives for polymer wetting may again be responsible. As shown by the LDPE datum, L/W forces are adequate to adsorb the neutral polymer on Monastral Green, but the pronounced polarity of CPE and EVA appears to reduce the ability of dispersive forces to stabilize these polymers in the adsorbed state. A possible reason may be the limited distance of approach in these cases, between adsorbing polymer segments and surface sites.

The attempt to identify contributions to the strength of adsorption bonds was based on the elution of adsorbates by *p*-xylene under reflux. In all cases, the samples to be eluted were covered by the plateau values of adsorbate, as given in Table II. The polymers were adsorbed from TCB, a strong solvent, but for elution the relatively weaker *p*-xylene was chosen so as to slow the kinetics of re-solution. This made possible a more detailed analysis of results, illustrated in Figure 2. There is nearly quantitative recovery of LDPE from all solids, as shown by the typical curves for LDPE/R-1 and LDPE/Chromosorb. In all cases, recovery of $>90\%$ of this adsorbate occurred in an elution period of 55 ± 5 min. That elution time is required to overcome the strength of L/W bonds; the parameter is designated as $t_{L/W}$ by the construction in Figure 2.

The contribution of non-dispersive, or acid-base forces, to the adsorption bond is evident in the data for EVA/R-3 and CPE/R-3. For the relatively weakly interacting pair, EVA/R-3, the total amount of polymer eluted is 81%, the remainder being held by specific interactions which resist the solvating power of *p*-xylene. Equilibrium attainment is slowed to an elution period near 100 min. A much more striking result was obtained for the strong acid-base combination of CPE/R-3. Here, equilibrium recovery of adsorbate occurred in an elution period of about 150 min, and the total quantity of CPE recovered was reduced to 58%. Adsorbed polymer at or very near the solid surface is held more tenaciously than are adsorbed layers further removed from the surface.

The implied relationship between acid-base interactions and the capacity of *p*-xylene to remove adsorbed polymer is confirmed by the data of Figure 3. Shown as a function of the Isp parameter is the percent polymer recovered in the time needed to overcome the L/W linkages between adsorbate and adsorbent. The existence of a strong correlation is evident. We may assume that similar patterns of results would be obtained for different choices of elution solvent. In other words, the position of curves in the coordinates of Figure 3 should depend quantitatively on the Flory χ value, that is

TABLE II
Plateau Adsorption and Isp Values for Polymer/Pigment Pairs

Polymer:	LDPE		EVA		CPE	
Solid:	Ads. (mg/M^2)	Isp	Ads. (mg/M^2)	Isp	Ads. (mg/M^2)	Isp
Rutile R-1	2.37	0	3.11	20.2	2.95	26.6
Rutile R-2	2.28	0	4.25	26.0	2.17	21.0
Rutile R-3	2.57	0	1.90	22.9	3.72	35.4
Mon. Green	2.45	0	1.18	7.0	1.02	3.7
Chromosorb®	1.20	0	1.06	4.5	0.93	3.5

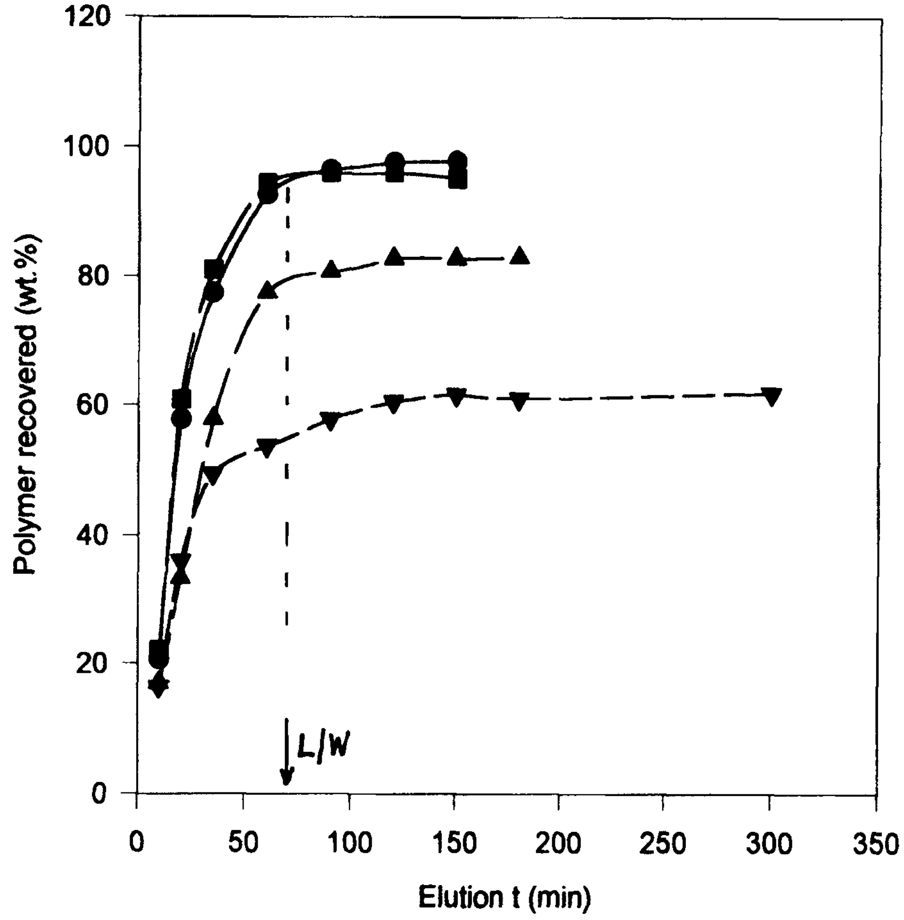

FIGURE 2 Recovery of polymer from adsorbed state by elution with p-xylene. ● LDPE from rutile R-1; ■ LDPE from Chromosorb; ▲ EVA from rutile R-3; ▼ CPE from rutile R-3.

on the thermodynamic interaction between the adsorbed polymer and the elution solvent.

3.3 Dispersion Stability

The stability of dispersions of solids in non-aqueous media is generally expressed by the principle of steric or entropic stabilization.[11,12] Briefly, unprotected particulates will tend to sediment or flocculate under the influence of gravity. An adsorbed polymer layer can confer stability if the close approach of particles entails the interpenetration of segments from adsorbed polymer chains and, consequently, a sufficiently large loss of entropy in the *solvated* segments of the adsorbed polymer. Accordingly, both the quantity and the architecture of the adsorbed polymer are vital elements in its performance as a stabilizing barrier.

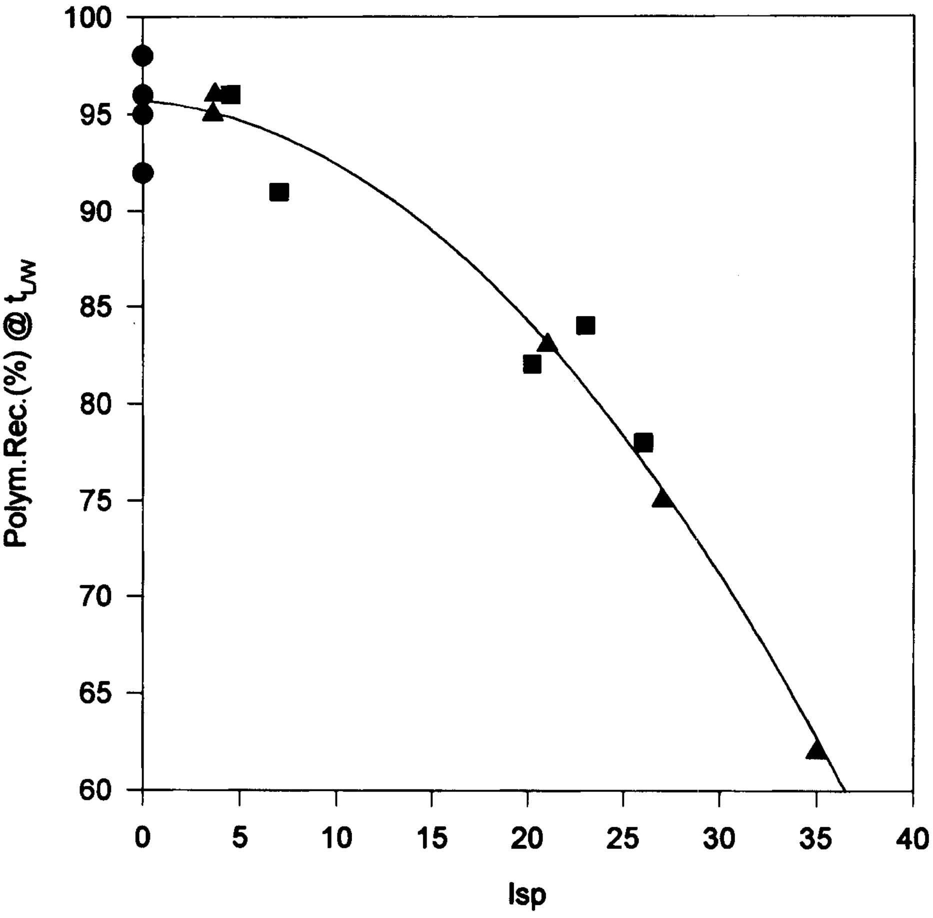

FIGURE 3 Dependence on acid/base interaction parameter of weight percent adsorbed polymer eluted from solids in time needed to overcome dispersive bonding. Polymer code: ● LDPE; ▲ CPE; ■ EVA.

The principle of entropic stabilization should apply to the present series of systems. The results reported in Figure 4 may be viewed from that standpoint. For clarity, only four of the polymer-solids combinations are represented. Evidently, although the ratio of solids to polymer was the same in all experimental trials, both the kinetics of solids deposition and the volumes occupied by sedimented particles varied broadly. The LDPE/R-1 and CPE/R-3 systems are considered to be poorly stabilized. Reference to Table II recalls that in both cases the quantity of adsorbed polymer is substantial. The limited stability of these dispersions must then be attributed to the configuration of the adsorbed polymer. In LDPE/R-1 only L/W forces can lead to polymer adsorption. In the presence of the strong solvent, TCB, it seems reasonable that polymer chains are anchored to a limited number of surface sites, with significant extension of the remaining free chain segments into the solvent. In this case, as solid particles approach each other, entanglement of extended chain segments seems a plausible event, resulting in the formation of aggregates which settle due to gravitational forces.

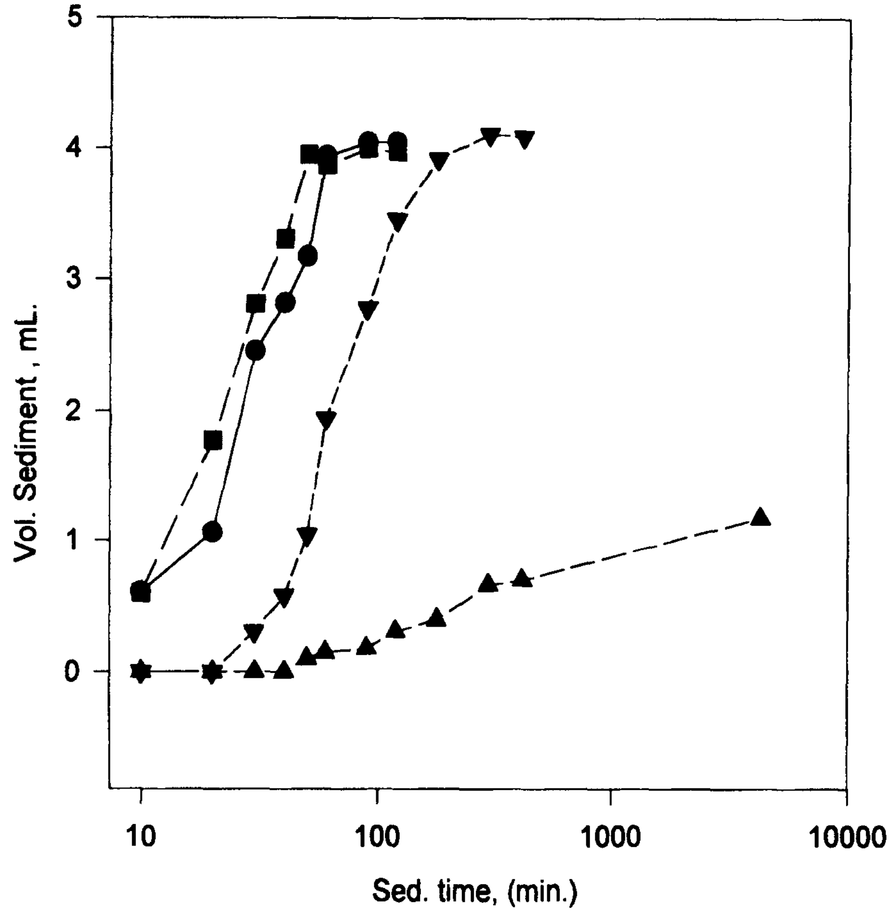

FIGURE 4 Effect of adsorbed polymer barrier on rate of solids settling in polymer solutions. System code: ● CPE/R-3; ▲ CPE/R-2; ▼ EVA/mon. green; ■ LDPE/R-1.

In the case of CPE/R-3, strong acid-base interactions would tend to flatten adsorbed polymer chains on the solid surface, and greatly restrict extension into the solvent medium. The flat configuration on adsorbate would generate a slight increase in the particle radius but, again, no appreciable barrier to particle aggregation and deposition. In contrast, the CPE/R-2 combination is well stabilized, with less than 10% of the available volume occupied by sedimented solids, following 7 days of observation. Table II shows that the mass of adsorbed polymer is appreciable if somewhat lower than for the other rutile adsorbents, and that the Isp value is considerably lower than for the CPE/R-3 pair. Multiple site adsorption of the polymer may be proposed, but with solvated chain segments looping into the continuum to form an effective entropic barrier to particle aggregation and deposition.

The qualitative description, above, suggests a complex relationship between dispersion stability and the strength of acid-base interactions as given by Isp for defined particulate-polymer pairs. The data in Figure 5 amplify on this. The total (equilibrium) volume of sediment following centrifugation was used to define the time required to deposit 50% of the equilibrium volume. This arbitrarily selected parameter was then plotted against Isp, showing that long-term stability of dispersions can be associated with definable limits of acid-base interaction. For Isp $\leqslant 15$, and again for Isp $\geqslant 30$, the dispersion stability is poor, with solids deposition to the level of comparison taking place in < 150 h. Between these ranges of Isp, however, excellent stability was obtained; indeed, in the three cases arrowed in Figure 5, the dispersion stability is essentially indefinite. It is stressed that the applicability of the diagram in Figure 5 is restricted to the current set of variables, including (at least) the solvent used, the degree of dispersion attained in the grinding process, and the laboratory conditions during sedimentation.

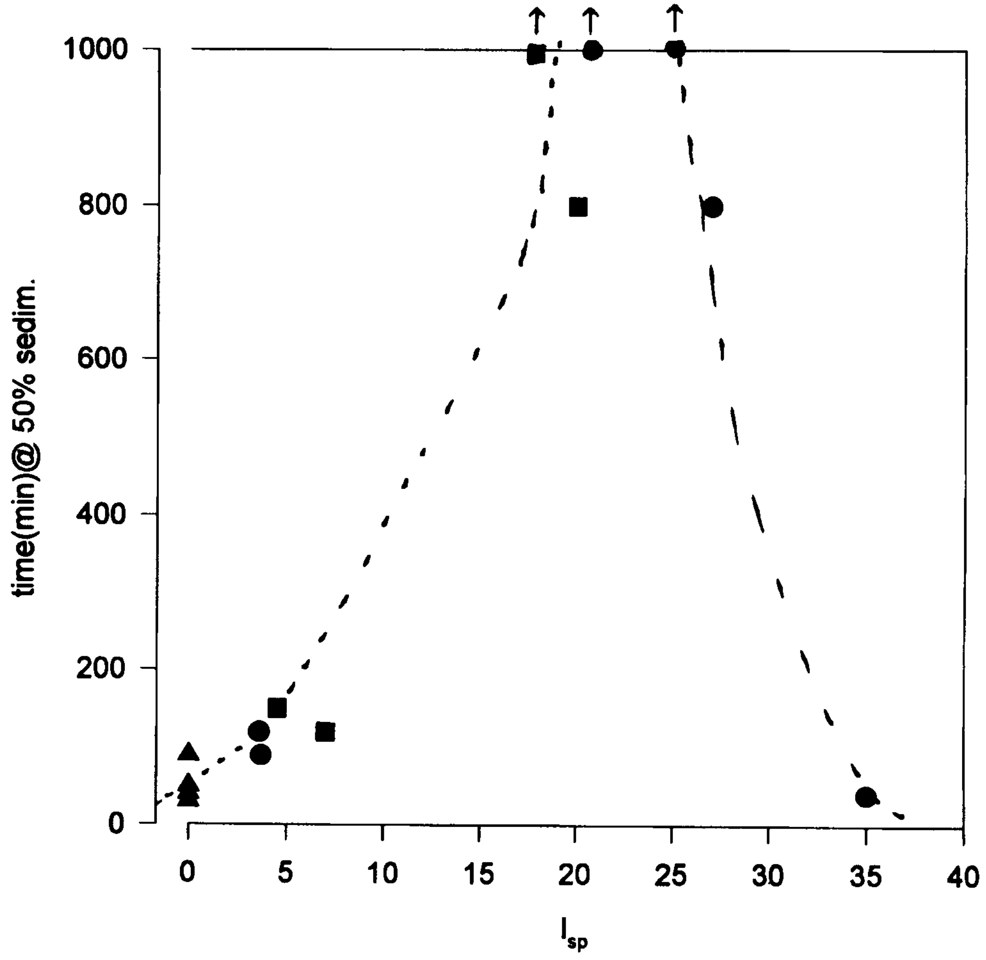

FIGURE 5 Acid-base interaction and the effectiveness of adsorbed polymer barriers as stabilizers of solids dispersed in polymer solutions. Ordinate is time required to sediment 50% of available solids. Polymer code: ▲ LDPE; ● CPE; ■ EVA.

Nevertheless, a general, quantifiable relationship is apparent between the configuration of adsorbed polymer molecules, and the balance of specific interaction forces among polymer, solvent and adsorbing solid surface. Since all quantities in that relationship are accessible experimentally, it is possible, in principle, knowledgeably to select (design) polymeric barriers for optimum performance of dispersed systems.

A final comment is made on apparent differences in the quality of deposited solids in the cases under discussion. Although solids deposited rapidly on either side of the range $15 < \mathrm{Isp} < 30$, those deposited in systems with Isp below that range tended to occupy greater volumes and to be more easily redispersed than deposits from systems with high Isp. Speculatively, the entanglement of extended adsorbed chains (at low Isp) results in flocculation, and the easy break up of loosely held sediment. At $\mathrm{Isp} > 30$, the solids, on contact, may be assumed to form more shear-resistant aggregates.

4. CONCLUSION

The following may be concluded from the study:

- Dispersive and acid-base interaction forces contribute to the adsorption of polymers onto dispersed solids. The existence of acid-base interactions increases the capacity of pigmenting solids for the adsorption of polymers from solution.
- Elution of polymers adsorbed on particulates has made it possible to separate the contribution of dispersive and acid-base forces to the stability of the bond at polymer/solid interfaces.
- The stability of solid dispersed in polymer solutions is dependent on interaction forces and can be expressed quantitatively as a function of the acid-base interaction between adsorbate/adsorbent pairs.
- Steric, or entropic mechanisms are responsible for the stabilization of the present solid/polymer combinations. A preferred range of acid-base pair interactions can be specified for dispersion stability; the applicability of the range, however, is restricted to the present study.
- The results of the study suggest that the experimental procedures followed may be of general use in the design of polymeric barriers for the stability of solids dispersions.

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