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STRATEGY FOR THE EVALUATION AND COMPATIBILIZATION OF PARTICULATE INCLUSIONS FOR USE IN MOLECULAR AND MACROMOLECULAR MEDIA

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ABSTRACT

The quality of the dispersion of particulate solids in low and high molecular weight media depends on the interfacial forces that govern the wetting and stabilization of the solids. An understanding of these forces enables rational selection of compatible powder–fluid systems, or signals the need to provide some compatibilizers to aid dispersion. In this paper we present a strategy for evaluating particle–fluid interactions based on assessing the stability of solids in a spectrum of low molecular weight fluids. For a coarse evaluation of the dispersibility tendencies, we show how these results can be visualized in terms of a three-dimensional graph in which partial solubility parameters are the coordinates. For a more refined evaluation of dispersibility, we extend the data analysis to two-

dimensional dispersibility maps in which donor and acceptor numbers of the fluids are coordinates. To exemplify the approach, experiments using three grades of titanium dioxide particles are presented. The methods are also sensitive enough to quantify the effects of surfactants added to compatibilize the titania particles with polyethylene.

INTRODUCTION

Particulate inclusions play many roles in a variety of technologically important applications. In low molecular weight vehicles such as those utilized for inks and coatings, particulate materials are used as pigments, UV protectors, and rheology modifiers, for example. When used in polymeric media, particulate inclusions are used for these same purposes and others, such as mechanical property enhancers and fillers. In all cases, the degree to which the particulate solids are dispersed governs the ultimate performance of the materials in which they are incorporated.

During material processing, the state of dispersion results from a dynamic balance between particle-particle forces and particle-matrix interactions. The dispersion of particulates into liquids can be categorized as involving three general phenomena.

First, the particles must be incorporated into the fluid medium. This requires favorable conditions for the wetting of the solids by the processing fluid, and hence knowledge of the interfacial interactions is necessary for enhancement of solids incorporation. Unfavorable interactions may result in the formation of particle agglomerates from solids that were unagglomerated before their incorporation within the processing fluid. These agglomerates usually degrade the characteristics of the suspension or composite.

The second stage involves the addition of mechanical energy to the system. In some cases (e.g., carbon black, silica), the particulate solids are supplied by the manufacturer in the form of agglomerates or pellets. In this case the processing goal is to disrupt these agglomerates to their elementary particles, or at least to fine fragments. The tendency of an agglomerate to resist disruption depends on the magnitude of cohesive forces acting between constituent particles. These forces result from van der Waals interactions, electrostatic effects, and the interplay between molecules (i.e., surfactants or binders) adsorbed onto the surfaces of the particles. A second role of the applied mechanical energy is to distribute fragments throughout the material.

The third aspect of dispersion is stabilization against reassociation of the particles which may be driven by the balance of the forces acting between the solids. One means to prevent reagglomeration is to deposit molecules onto the surface of dispersed particles which can provide a steric barrier to particle-particle approaches. In macromolecular fluids the formation of "bound polymer" is indicative of a successful stabilization against reagglomeration.

Interfacial interactions between particles, between the particles and the processing fluid, and between particles and secondary species strongly determine the dispersibility characteristics of the solids in various media. In this paper we focus on the wetting and stabilization stages of the dispersion processes since both deal strictly with chemical interactions. The reader is referred to the literature [e.g.,

Refs. 1–3] for studies of the interplay between mechanical and chemical effects as they influence the disruption stage.

The thermodynamics of the wetting process are briefly reviewed in the sections which follow. Depending on the nature of the medium, different classes of forces may play the dominant role in governing wetting. For instance, in low molecular weight media, specific interactions (i.e., acid–base, polar interactions) between the solids and processing fluids may be more important than dispersive interactions (i.e., van der Waals interactions). The reverse may be true for dispersions in macromolecular fluids. One goal of this paper is to provide some guidance in understanding the relative importance of the various types of interactions.

In this paper we also present an experimental methodology for assessing the tendency of specific particles to disperse well in a given processing medium. In principle, information about particle dispersibility in low molecular weight media can be translated to macromolecular fluids of equivalent thermodynamic behavior. This behavior can be characterized in terms of the solubility parameters or acceptor/donor numbers. The method is exemplified by studying the dispersibility of titanium dioxide powders having a variety of surface characteristics. Dispersibility in both low and high molecular weight fluids is examined. The usefulness of incorporating surface-active agents to alter the interfacial behavior of these powders is also briefly studied. These results should be useful for those attempting to tailor a specific particle–fluid system.

GENERAL EVALUATION OF POWDER–FLUID INTERACTIONS

To model the energetics of powder–fluid interactions, we adopt concepts first proposed to model similar interactions between solvents. The solubility parameter, δ , is an intrinsic measure of the intermolecular interactions within solvents [4]. For dilute mixtures of solvent 2 in solvent 1, the heat of mixing, ΔH_{mix} , can be written as

$$\Delta H_{\text{mix}} = V_2 \phi_1^2 (\delta_1 - \delta_2)^2 \quad (1)$$

where ϕ_1 is the volume fraction of solvent 1 and V_2 is the molar volume of solvent 2.

Burrell [5] suggested that the molecular interactions controlling solubility, miscibility, adhesion, and dispersion are all similar. Thus, we adopt the form of Eq. (1) to model the energetics of the powder dispersion process:

$$\Delta H_{\text{p,dis}} = V_p \phi_s^2 (\delta_s - \delta_p)^2 \quad (2)$$

where subscripts s and p refer to solvent and powder, respectively.

For good incorporation of the powder into a fluid, $\Delta H_{\text{p,dis}}$ should be small relative to the entropic contribution from dispersion, i.e., fluids that have solubility parameters comparable to that of the solid have favorable energies of wetting.

Hansen [6] attributed the solubility parameter to three distinct contributions: dispersive interactions (δ_d), polar interactions (δ_p), and hydrogen bonding interactions (δ_h). The total solubility parameter (δ_t) is assumed to be the combination of these three partial components [6–9]:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

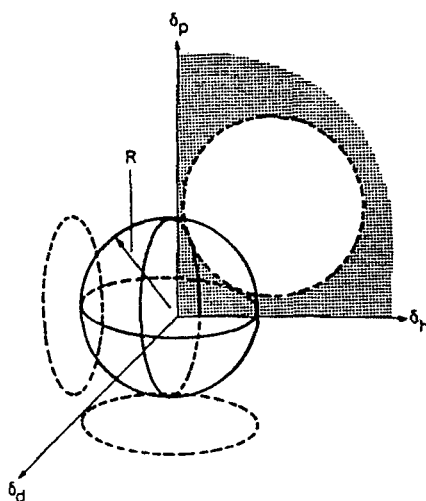


FIG. 1. Three-dimensional representation of the solubility parameter.

Depending on the nature of the medium, different interactions may play the dominant role in governing particle wetting and, implicitly, suspension stability. Using a three-dimensional mapping in which the partial solubility parameters are the coordinates, one can define a suspension stability region encompassing the various media that wet the particle well [8, 10, 11]. The location and the characteristic size of the solubility region will reflect the powder surface characteristics (Fig. 1).

In this paper this method is exemplified by studying the dispersibility in a variety of media of titanium dioxide powders having different surface characteristics. The powders were three experimental grades of rutile titanium dioxide kindly supplied by Kerr-McGee Corporation. For convenience, the powders will be denoted Ti-A through Ti-C. The powders were dried at 200°C for 24 hours and stored

TABLE 1. Properties of Powders

Property	Ti-A	Ti-B	Ti-C
Particle size ^a (μm)	0.167	0.161	0.156
BET surface area ^b ($\text{m}^2 \cdot \text{g}^{-1}$)	9.4	14.7	12.8
Surface treatment ^b	None	Al	Al + Si
Si/(Al + Si) ratio ^b		0	0.52
Remark ^b	SiO ₂ < 0.2%		
Surface tension, ^c γ_p^d ($\text{dyn} \cdot \text{cm}^{-1}$)	111.8	149.6	77.5
Donor number, ^c DN_p ($\text{kcal} \cdot \text{mol}^{-1}$)	24.1	20.6	18.1
Acceptor number, ^c AN_p	34.3	24.1	34.0

^aMeasured by SEM and image analysis.

^bData from manufacturer.

^cUsing IGC measurement from Ref. 23.

in a dessicator before use. Some of their important properties are summarized in Table 1.

We studied the suspension stability in a variety of solvents whose properties are summarized in Table 2. The solvents used were of spectroscopic or analytical grade. Distilled and deionized water were also used.

Sedimentation tests were used to judge suspension stability. Flocculation of particles due to poor wetting and/or lack of a barrier to prevent coagulation results in faster settling solids. Flocculated dispersions give a loose sediment and a clear supernatant resulting from the sweeping of particles from the dispersion by the settling flocculates. Conversely, sedimentation of a well dispersed system will give a high density compact, with some small particles possibly remaining in suspension (cloudy supernatant). The scale used to judge the stability of the suspension was defined in terms of the characteristics of the supernatant during the sedimentation and the time for the sediment volume to reach a given value (Table 3).

The suspension stability of the powders is presented in Fig. 2. The stability data are plotted using the partial solubility parameters of the solvents as coordinates. The three powders show similar stability regions and identical coordinates for the center of the stability sphere. All three powders show very good stability in polar solvents and poor stability in nonpolar solvents.

Although pointing out the general characteristics of particle surface (in this case hydrophilic characteristics), the stability spheres do not discriminate between the more specific features of powder interactions with various solvents. A more refined evaluation is required in order to assess the dispersibility of powders in these solvents.

DETAILED EVALUATION OF PARTICLE-FLUID INTERACTIONS

The dispersion of particulates into fluids can be viewed as being affected by two different types of powder-solvent interaction. The first is a dispersive interaction which can be quantified in terms of a Hamaker constant [12] or the dispersive component of the surface tension [13].

The second is an acid/base specific interaction which affects the energetics of the dispersion process. In view of the above, Eq. (2) can be modified to include the combination of polar and hydrogen bonding interactions in terms of the donor-acceptor concept addressed by Gutmann [14, 15]. Thus:

$$\Delta H_{p,dis} = V_p \phi_s^2 (\delta_{sd} - \delta_{pd})^2 + k(AN_s - AN_p)(DN_s - DN_p) \quad (4)$$

Here, k is a scaling constant, AN is the acceptor number, DN is the donor number, and the subscripts p and s refer to the powder and solvent, respectively. For convenience, we denote the dispersive part of Eq. (4), $V_p \phi_s^2 (\delta_{sd} - \delta_{pd})^2$, as ΔH_d , while the acid/base component of Eq. (4) is abbreviated as ΔH_{ab} .

For inorganic powders in polar solvents, the dispersive interaction ΔH_d is small relative to the specific interaction and does not significantly vary with the suspending medium [10]. Thus, the energy of dispersion is often determined primarily by ΔH_{ab} . Accordingly, if ΔH_{ab} is smaller than some fixed value ΔH^* , there will be favorable powder-solvent interactions [16]. For dilute suspensions, neglect-

TABLE 2. Solvent Properties

No.	Solvent	δ_d^a (cal/cm ³) ^{1/2}	δ_p^a (cal/cm ³) ^{1/2}	δ_h^a (cal/cm ³) ^{1/2}	δ_t^a (cal/cm ³) ^{1/2}	η^b (T, °C), cP	ρ^b (T °C), g/cm ³
1	n-Heptane	7.48	0.00	0.00	7.48	0.40 (25)	0.68 (20)
2	n-Nonane	7.72	0.00	0.00	7.72	0.67 (25)	0.71 (20)
3	Diethyl ether	7.09	1.42	2.49	7.72	0.23 (20)	0.71 (20)
4	Methyl isobutyl ketone	7.48	2.98	2.00	8.31	0.58 (20)	0.80 (20)
5	Ethyl acetate	7.72	2.59	3.52	8.85	0.46 (20)	0.90 (20)
6	m-Xylene	8.06	3.52	1.17	8.89	0.60 (25)	0.86 (20)
7	Toluene	8.80	0.70	0.98	8.90	0.55 (25)	0.87 (20)
8	Benzene	7.87	4.20	2.00	9.14	0.61 (25)	0.89 (16)
9	Methyl ethyl ketone	7.82	4.40	2.49	9.28	0.42 (21)	0.81 (20)
10	Tetrahydrofuran	8.21	2.79	3.91	9.48	0.55* (20)	0.89 (20)
11	Acetone	7.57	5.08	3.42	9.78	0.32 (25)	0.79 (20)
12	Dichloromethane	8.89	3.08	2.98	9.92	0.41 (25)	1.32 (25)
13	n-Octanol	8.31	1.61	5.82	10.26	7.21 (25)	0.83 (20)
14	Nitrobenzene	9.77	4.20	2.00	10.85	2.02 (20)	1.20** (20)
15	n-Butanol	7.82	2.79	7.72	11.29	2.61 (25)	0.81 (20)
16	Isopropanol	7.72	2.98	8.01	11.49	1.77* (30)	0.79 (20)
17	Nitromethane	7.72	9.19	2.49	12.27	0.63 (25)	1.14 (20)
18	Dimethylsulfoxide	8.99	8.02	4.99	13.05	2.00* (25)	1.10 (20)
19	Methanol	7.38	6.01	10.90	14.47	0.55 (25)	0.79 (20)
20	Formamide	8.41	12.8	9.29	17.9	3.30 (25)	1.13* (20)
21	Water	7.63	7.82	20.68	23.87	0.90 (25)	0.99 (20)

^aFrom Ref. 24 (25°C).^bFrom Ref. 26, except * from Ref. 27 and ** from Ref. 28.

TABLE 3. Stability Scale

Supernatant characteristics ^a	Settling time ^b	Stability scale
Clear	Less than 30 minutes	Unstable 1 (U1)
Slightly cloudy	Less than 30 minutes	Unstable 2 (U2)
Cloudy	30 minutes–24 hours	Moderately stable (M)
Cloudy	More than 24 hours	Stable (S)

^aAt 30 minutes.

^bTo reach a sediment volume of 20% of the initial suspension volume.

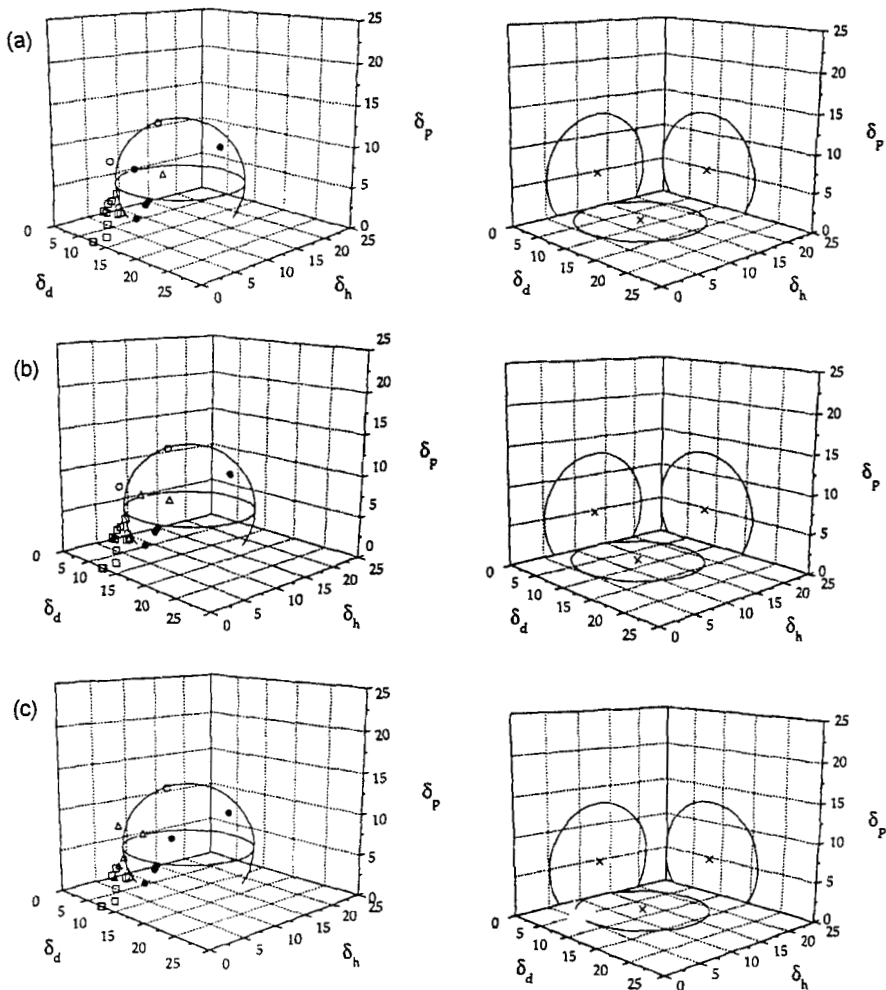


FIG. 2. Solubility parameter spheres for the as-received powders: (a) Ti-A, (b) Ti-B, (c) Ti-C. Key: ●, stable (S); ○, moderately stable (M); △, unstable 2 (U2); □, unstable 1 (U1) [δ in $(\text{cal}/\text{cm}^3)^{1/2}$].

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ing the energetics of powder–powder interactions, the condition of favorable powder–solvent energetics can be expressed as

$$DN_s(AN_s - AN_p) \leq \Delta H^*/k + DN_p AN_s \quad (5)$$

The value of $\Delta H^*/k$ must be determined empirically. Equation (5) can be used to prepare dispersibility maps in terms of acceptor and donor numbers for the solvents.

The method is exemplified by studying the dispersibility of the three titanium dioxide powders listed in Table 1 in a variety of solvents. The properties of these solvents are summarized in Table 4. Acceptor and donor numbers for polymers can be determined through standard techniques such as inverse gas chromatography. The solvents can be classified into four main categories depending on the combination of their donor and acceptor numbers.

Neutral solvents such as the alkanes and aromatics have relatively low acceptor and donor numbers. In this case the contribution of the acid/base interaction to the overall heat of dispersion is small, leaving the dispersive interaction to control the dispersion stability. Indeed, the titanium dioxide powders were unstable in neutral solvents.

Solvents that have both large acceptor and donor numbers are termed amphoteric solvents. Since most solvents have limited acidity and basicity, few fall into this category.

Acidic solvents are characterized by large acceptor numbers and small donor numbers. Basic solvents have large donor numbers but small acceptor numbers. For these fluids, ΔH_{ab} can take on large negative values, indicating the possibility of good interaction between the powders and dispersion media. In general, acidic powders exhibit better stability in basic solvents and vice versa.

Figure 3 shows the dispersibility maps for the three titanium dioxide powders examined. A least-squares optimization technique was used to determine the values of $\Delta H^*/k$, DN_p , and AN_p that give the critical energy boundary defined as the condition of equality in Eq. (5). Those solvents giving unstable dispersions and located closest to the origin on the acceptor/donor number mapping were denoted as key solvents. Identification of key solvents is subjective, but examination of the whole dispersibility map will usually enable their reliable selection.

To find the optimum fitting parameters, combinations of values of $\Delta H^*/k$ (0–20 kcal·mol⁻¹ in increments of 0.1 kcal·mol⁻¹), AN_p (0–100 in increments of 0.5), and DN_p (0–100 kcal·mol⁻¹ in increments of 0.5 kcal·mol⁻¹) were used to predict the location of the critical energy curve. The goodness of fit was judged by computing the sum of squared error (deviation between the predicted and actual donor numbers at a given acceptor number) for the key solvents. Variations in the value of ΔH_d between different solvents were neglected. The curves shown on the dispersibility maps in Fig. 3 correspond to the globally best fit. The curve-fitting procedure was found not to be overly sensitive to the choice of key solvents.

Examination of the dispersibility maps shows that some solvents located outside the critical energy curve were poorly dispersing. In these cases, powder–powder interactions have led to agglomeration, even though the energetics of the dispersion process favor good wetting of the powders by the solvents. Powder–powder interactions result from a combination of van der Waals attractive forces and electrostatic

TABLE 4. Properties of Solvents

Solvent (symbol)	Viscosity ^a η , cP	Dielectric constant ^b ϵ	Donor number ^c DN_s (kcal·mol ⁻¹)	Acceptor number ^c AN_s
Propan-2-ol (iPrOH)	2.08	18.3	36.0	33.5
Ethanol (EtOH)	1.10	24.3	32.0 ^e	37.1
Methanol (MeOH)	0.55	32.6	19.0 ^e	41.3
Water (Wa)	0.89	80.4	18.0	54.8
Acetic acid (AcOH)	1.15	6.2	10.5 ^f	52.9
Dimethylsulfoxide (DMSO)	1.96	46.6 ^d	29.8	19.3
Dimethylformamide (DMF)	0.80	36.7 ^d	26.6	16.0
Acetone (AC)	0.32	20.7	17.0	12.5
Benzylaldehyde (BA)	1.23	17.8	16.0 ^e	12.8 ^f
Nitrobenzene (NB)	1.98	34.8	11.0 ^e	14.8
Nitromethane (NM)	0.62	35.9 ^d	2.7	20.5
<i>n</i> -Hexane (C6)		1.9	0.0	0.0
Benzene (Bz)		2.3	0.1	8.2
Toluene (To)		2.4	3.9 ^f	3.3 ^f
Xylene (Xy)		2.6	4.8 ^f	2.4 ^f
Diethyl ether (DEE)		4.3	19.2	3.9
Ethyl acetate (EAc)		6.0	17.1	9.3 ^f
Butyl acetate (BAc)		5.0	15.0 ^e	5.1 ^g
Tetrahydrofuran (THF)		7.6 ^d	20.0	8.0
Methyl ethyl ketone (MEK)		18.5	17.4 ^e	12.9 ^f
Diethyl ketone (DEK)		17.0	15.0 ^e	12.5 ^g
Chloroform (CF)		4.8	0.0 ^e	23.1
Methylene chloride (MC)		9.1	1.0 ^e	20.4
<i>n</i> -Butanol (BuOH)		17.5	29.0 ^e	36.8 ^f
Formamide (FA)		109.0	36.0 ^e	39.8

^aMeasured by Ostwald viscometer at 25°C.

^bFrom Ref. 29 unless marked otherwise.

^cFrom Ref. 14 unless marked otherwise.

^dFrom Ref. 27.

^eFrom Ref. 30.

^fFrom Ref. 31.

^gCalculated from $\log \epsilon = 0.0711AN + 0.0054DN + 0.2581$ from Ref. 31.

double-layer repulsive forces. Sufficient electrostatic interaction is necessary to insure adequate dispersion stability.

Surface charge can be generated upon contacting powders with solvents through either proton transfer [17], electron transfer [18], or adsorption/desorption of ionic species. Labib and Williams [19, 20] explained how the charging

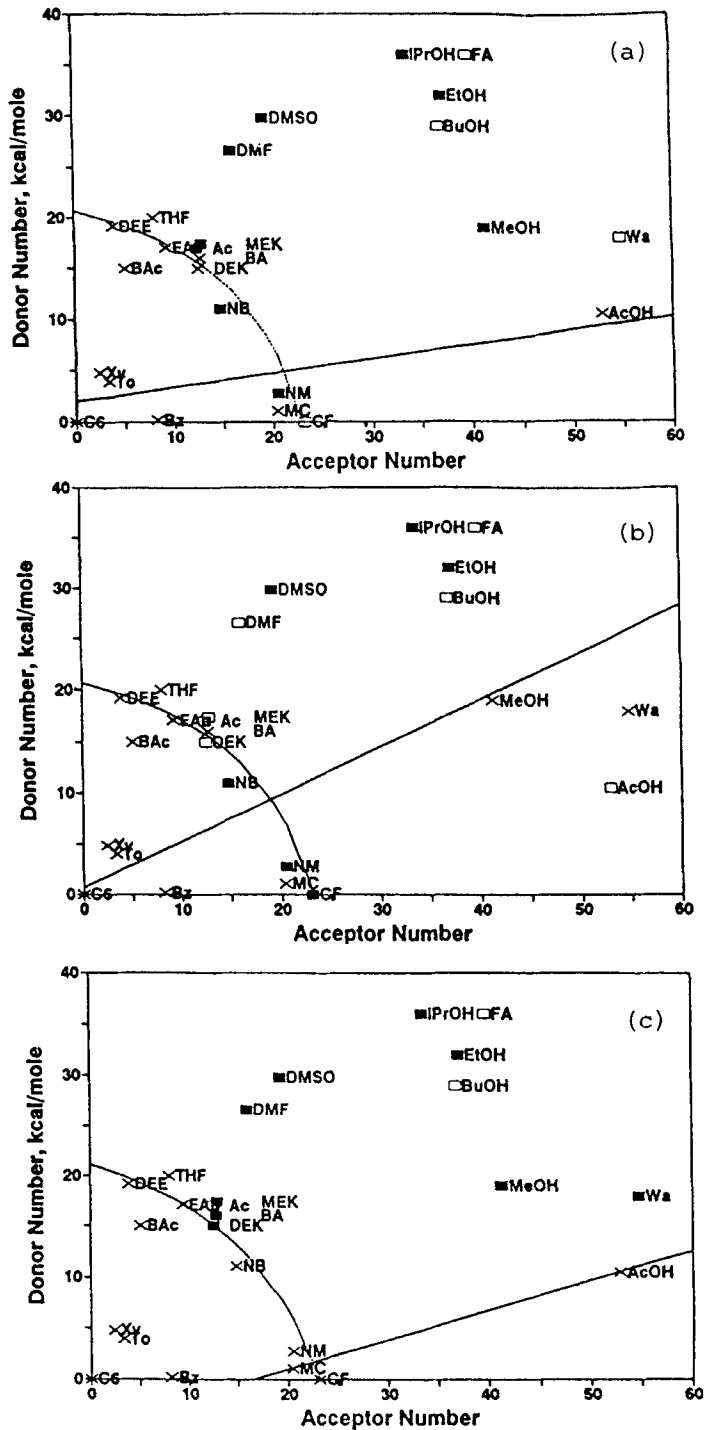


FIG. 3. Dispersibility maps of (a) Ti-A, (b) Ti-B, (c) Ti-C. Key: x, unstable; □, moderately stable; ■, stable.

TABLE 5. Zeta Potentials (mV) of Powders in Organic Solvents

Solvents	Ti-A	Ti-B	Ti-C
Propan-2-ol	-81.7	-70.8	-81.2
Ethanol	-48.7	-76.4	-42.4
Methanol	-43.6	-14.0	-43.9
Water (pH 7)	-57.0	8.0	-50.0
Acetic acid	18.7	101.2	22.2
Dimethylsulfoxide	-88.3	-75.9	-67.3
Dimethylformamide	-45.7	-61.8	-77.7
Acetone	-37.5	-47.8	-64.0
Benzylaldehyde	-50.1	-28.5	-54.4
Nitrobenzene	-43.2	-43.6	-25.4
Nitromethane	31.6	35.5	11.1

behavior is related to the surface acidity and the electron transfer between powder and solvent. Since titanium dioxide powders contain amphoteric surface hydroxyl groups [21, 22], the state of surface charge and the zeta potential depend on the acidity of the dispersing solvents.

Following Jensen [15], we assume that the zeta potential ζ can be correlated by

$$\zeta = \zeta_0 + \alpha DN_s + \beta AN_s \quad (6)$$

where ζ_0 is a reference zeta potential (corresponding to that exhibited by the powder in a neutral or noninteracting solvent such as an alkane), and α and β are base and acid sensitivity factors, respectively. The zeta potentials of these titanium dioxide powders in a variety of solvents [23] are summarized in Table 5. Table 6 gives the results of fitting the zeta potential results to the form predicted by Eq. (6).

Superimposed on the maps in Fig. 3 are lines depicting zero zeta potential from Eq. (6). The overall dispersibility can be viewed to result from both powder-solvent interactions and powder-powder interactions. Two conditions must be met for the formation of a stable dispersion. First, there must be favorable energetics for the wetting of the solid by the solvent. This corresponds to choosing a fluid located outside of the critical energy of dispersion curve on the dispersibility map.

TABLE 6. Parameters for Zeta Potential Correlation

Parameter	Ti-A	Ti-B	Ti-C
Base sensitivity factor α (mV·mol·kcal ⁻¹)	-2.89	-4.16	-2.61
Acid sensitivity factor β (mV)	0.40	1.92	0.76
Reference zeta potential ζ_0 (mV)	5.71	2.66	-12.73
Correlation coefficient	0.679	0.858	0.728

Second, the net powder–powder interaction force must be sufficiently repulsive to provide suspension stability. This corresponds to avoiding solvents located within a band of low zeta potential.

Comparison of the dispersibility maps in Fig. 3 illustrates the effect of powder surface treatment. Grade Ti-B disperses well in acidic solvents; this is consistent with the alumina surface rendering it a relatively basic powder. Grades Ti-A (minimally treated) and Ti-C (proportionately treated with silica and alumina) show good dispersibility in both acidic and basic solvents.

The dispersibility maps plotted in terms of acceptor and donor number coordinates are more sensitive to modifications in surface acidity of the powders than the stability spheres drawn based on the partial solubility parameters. Superposition of a zero zeta-potential line on the dispersibility map augments the interpretation of dispersion stability.

COMPATIBILIZATION FOR USE IN POOR DISPERSING MEDIA

Most inorganic powders show hydrophilic surface characteristics and consequently poor dispersion behavior in nonpolar media. The adsorption of surface-active agents or polymers onto such particulates should render the surface more hydrophobic and thus enhance dispersibility in organic media.

To exemplify the use of surfactant treatment for enhanced dispersibility, we used anionic surfactants to compatibilize titanium dioxide with polyethylene. Our strategy involves choosing surfactants with hydrophobic tail(s) matching closely the solubility parameter of polyethylene [$\delta_{\text{dPE}} = 8.6 \text{ (cal/cm}^3)^{1/2}$, $\delta_{\text{pPE}} = 0.0$, $\delta_{\text{rPE}} = 0.0$] [24].

The surfactants used in our study were sodium di(2-ethyl hexyl) sulfosuccinate (AOT), sodium dodecyl benzene sulfonate (SDBS), and sodium dodecyl sulfate (SDS) from Aldrich Co. The chemical formula and some properties of the surfactants are shown in Table 7.

Surfactant was adsorbed from aqueous solutions onto the different powders. The initial surfactant concentration was chosen based on the adsorption isotherms previously determined [25]. This concentration was chosen in the adsorption plateau region in order to insure that the powder particles are maximally covered by the surfactant layer. The coated powders were dried at 100°C (24 hours), and the

TABLE 7. Anionic Surfactants

Surfactant	Chemical formula	MW, g/mol	$\delta_{\text{tail,}}^{\text{a}}$ (cal/cm ³) ^{1/2}
AOT	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OOCCH}(\text{SO}_3\text{Na})\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$	444	8.2
SDBS	$\text{C}_{12}\text{H}_{25}(\text{C}_6\text{H}_5)\text{SO}_3\text{Na}$	348.5	8.8
SDS	$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	288	8.1

^aCalculated based on chemical structure.

agglomerates were broken up and screened using a 50-mesh sieve. The fine particles were dried again for 24 hours.

The suspension stability of the surfactant-treated TiO_2 powders in different liquids are presented in Figs. 4–6. A comparison with Fig. 2 shows that in all the cases studied the surfactant treatment shifts the center of the stability sphere to smaller values in the polar and hydrogen bonding components, which should render the powder more compatible with polyethylene. The effectiveness of the surfactant treatment was quantified by calculating the distances between the point representing the solubility parameter of polyethylene and the boundary of the stability sphere. The results are summarized in Table 8.

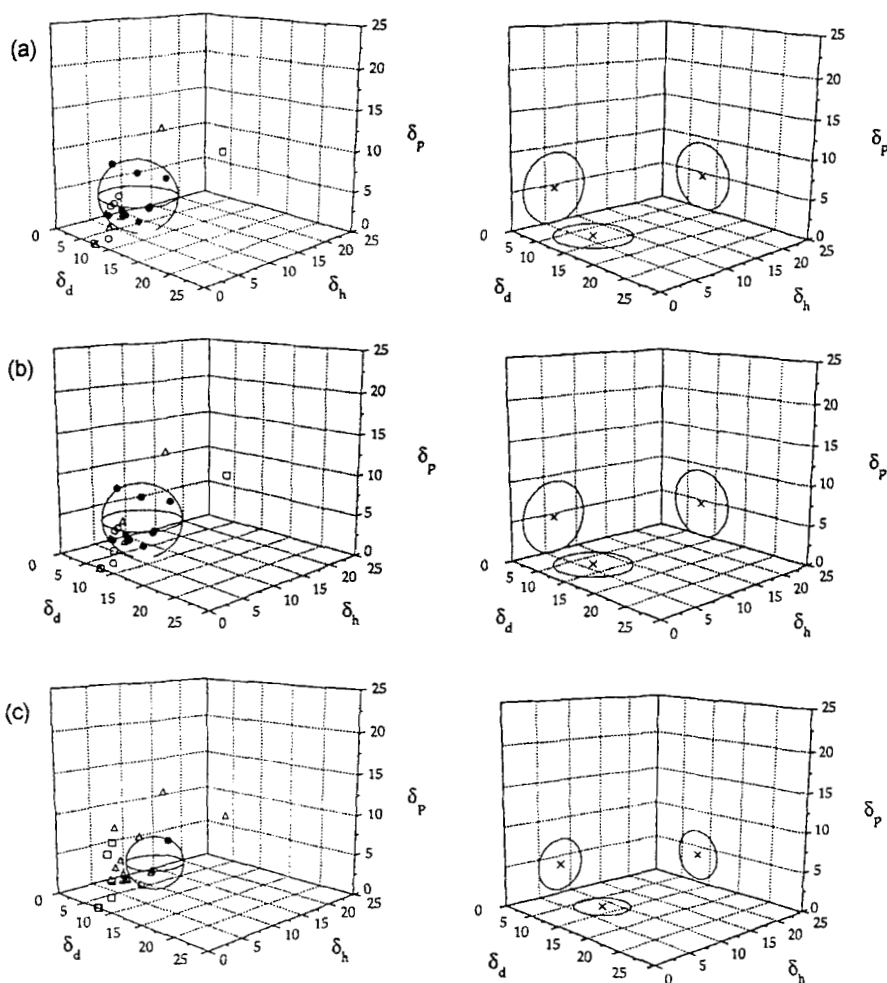


FIG. 4. Solubility parameter spheres for the AOT treated powders: (a) Ti-A, (b) Ti-B, (c) Ti-C. Key: ●, stable (S); ○, moderately stable (M); △, unstable 2 (U2); □, unstable 1 (U1) [δ in $(\text{cal}/\text{cm}^3)^{1/2}$].

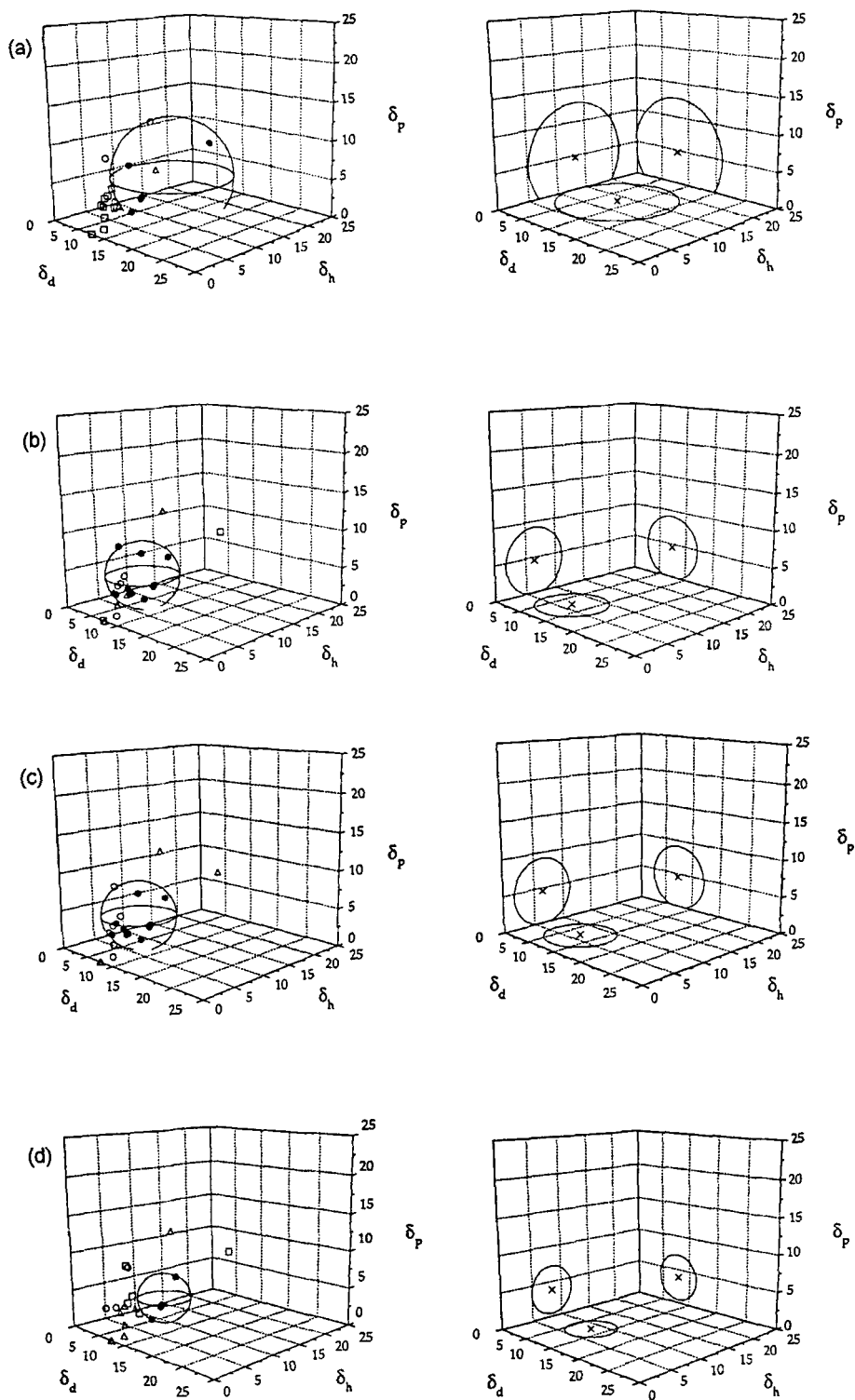


FIG. 5. Solubility parameter spheres for the Ti-B treated with different surfactants: (a) no surfactant treatment, (b) AOT, (c) SDBS, (d) SDS. Key: ●, stable (S); ○, moderately stable (M); △, unstable 2 (U2); □, unstable 1 (U1) [δ in $(\text{cal}/\text{cm}^3)^{1/2}$].

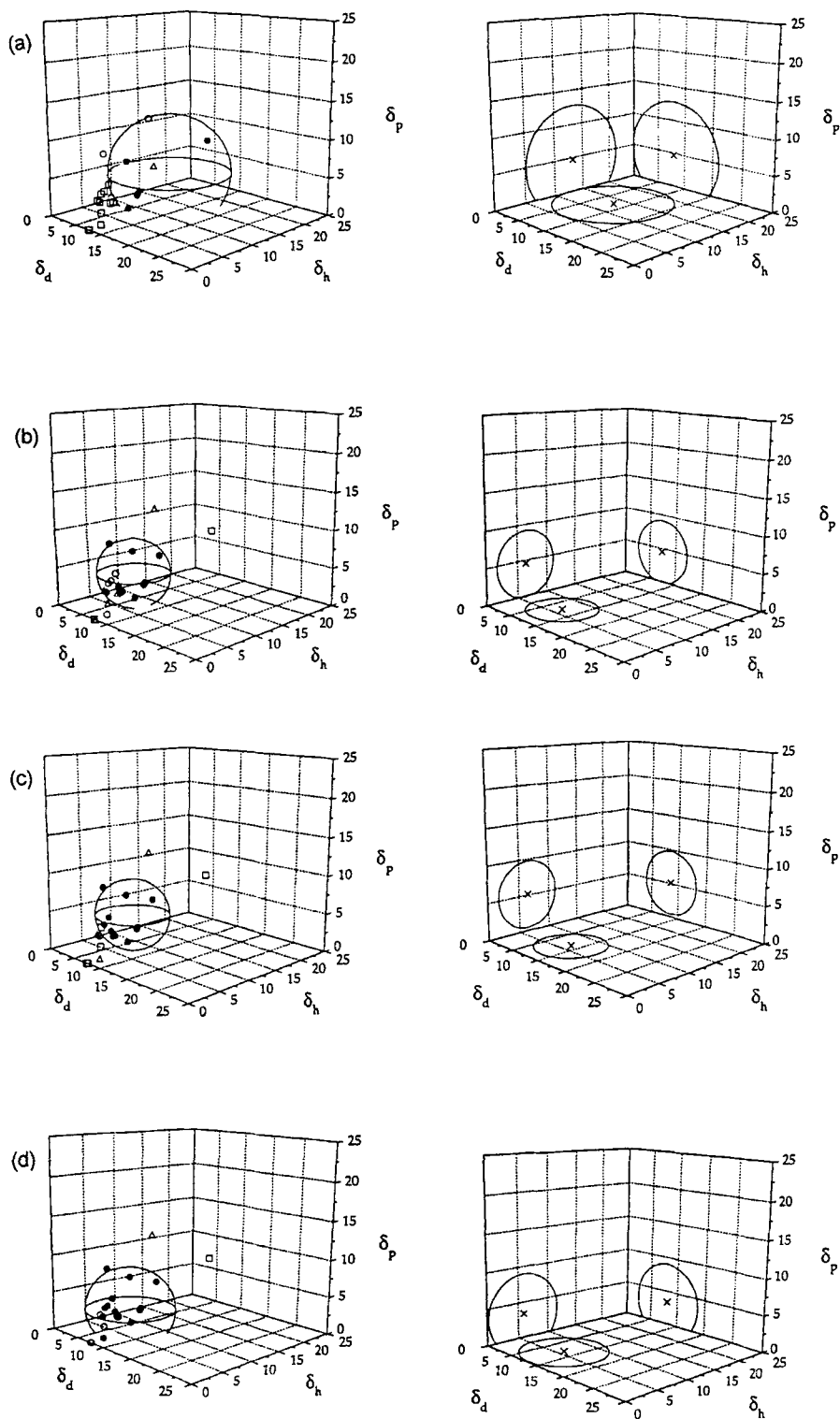


FIG. 6. Solubility parameter spheres for AOT treated Ti-B particles: (a) no surfactant treatment, (b) $C_0 = 5 \times 10^{-3}$ M, (c) $C_0 = 1.5 \times 10^{-3}$ M, (d) $C_0 = 5 \times 10^{-3}$ M and $C_{\text{HCl}} = 2 \times 10^{-3}$ M. Key: ●, stable (S); ○, moderately stable (M); △, unstable 2 (U2); □, unstable 1 (U1) [δ in $(\text{cal}/\text{cm}^3)^{1/2}$].

TABLE 8. Three-Dimensional Solubility Parameters for the Powders

System	δ_{d0} (cal/cm ³) ^{1/2}	δ_{p0} (cal/cm ³) ^{1/2}	δ_{h0} (cal/cm ³) ^{1/2}	δ_t (cal/cm ³) ^{1/2}	S (cal/cm ³) ^{1/2}
Ti-A	7.97	4.71	13.25	16.17	6.02
Ti-B	7.97	4.71	13.25	16.17	6.02
Ti-C	7.97	4.71	13.25	16.17	6.02
Ti-A-AOT	7.43	4.50	6.45	10.82	3.25
Ti-B-AOT	7.43	4.50	6.45	10.82	3.25
Ti-C-AOT	7.84	3.81	8.36	12.08	5.83
Ti-A-SDBS	7.43	4.50	6.45	10.82	3.25
Ti-B-SDBS	7.43	4.50	6.45	10.82	3.25
Ti-C-SDBS	8.14	4.55	6.94	11.62	4.03
Ti-A-SDS	8.02	2.30	6.91	10.03	5.99
Ti-B-SDS	7.84	3.81	8.36	12.08	5.83

The effect of surfactant treatment on the powder-polymer interactions was also investigated through determination of bound polymer in dispersions of titania particles in polyethylene. Linear low density polyethylene (LLDPE) GA 584 ($\eta = 110 \text{ Pa}\cdot\text{s}$ at 170°C) from Quantum Chemical Corporation was used in the experiments.

The polyethylene composites were prepared using a rotating cone and plate device (106 mm diameter and 4° cone angle) built in our laboratory. The device is mounted within a temperature-controlled oven. Pigment agglomerates ($< 300 \mu\text{m}$) were dry blended with the polymer pellets (LLDPE) and melted at 200°C in a vacuum oven. The dispersion of the powder particles in the cone and plate device was carried out at 170°C and a shear rate of 19.5 s^{-1} for 30 minutes. The final mixture was molded to form a $0.8 \pm 0.05 \text{ mm}$ sheet. A small sample ($\approx 0.1 \text{ g}$) of

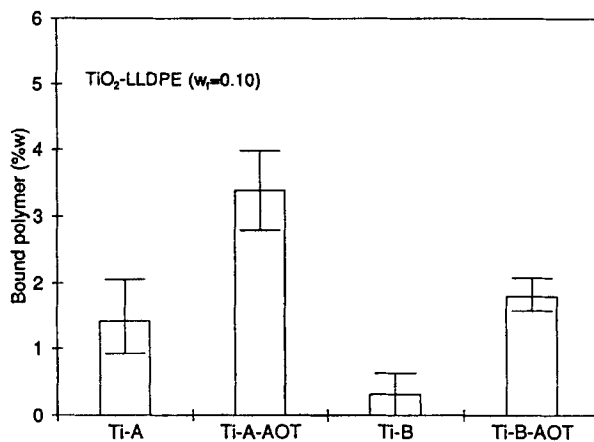


FIG. 7. Effect of the AOT surfactant treatment on the amount of bound polymer.

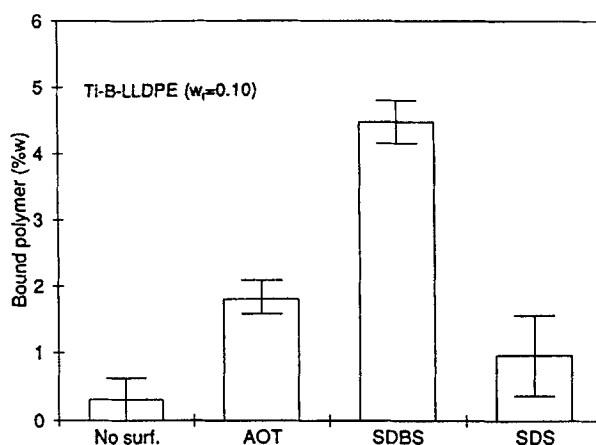


FIG. 8. Effect of the surfactant treatment on the amount of bound polymer.

the composite was charged in a flask with 25 mL *m*-xylene. The free polymer was extracted while heating the system, and after the free polymer was dissolved, the suspended filler particles were filtered using a nylon membrane of 0.45 μm pore size. The membrane was then dried in a vacuum oven and a gravimetric technique was used to quantify the amount of bound polymer. The titania content of the composite was determined by burning a separate polymer sample at 800°C and weighing the residual ash.

The effect of the AOT treatment on the bound polymer (relative to the total polymer in the composite) is presented in Fig. 7. The amount of bound polymer increases with surfactant treatment, reflecting better interfacial interactions between the polymer molecules and the filler particles.

The amount of bound polymer for the different Ti-B systems is shown in Fig. 8. In all cases the surfactant treatment increases the amount of bound polymer compared with the bare powder, which corresponds to the shifts of the stability spheres toward the location of the LLDPE solubility parameter. SDBS, with a tail solubility parameter closest to that of polyethylene, seems to be the most effective between the surface-active agents investigated.

CONCLUSIONS

In this paper we presented a strategy for the evaluation of particle dispersibility in various media. The strategy is based on observing the stability of suspensions in low molecular weight media. This information can be used to predict particle interactions with macromolecular media of known thermodynamic behavior. This method is sensitive enough to discriminate between slight variations in surface chemistry. Shifts induced by the use of surfactants in interfacial properties can also be monitored by this technique.

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REFERENCES

- [1] I. Manas-Zloczower, A. Nir, and Z. Tadmor, *Rubber Chem. Technol.*, **55**, 1250 (1982).
- [2] S. P. Rwei, I. Manas-Zloczower, and D. L. Feke, *Polym. Eng. Sci.*, **31**, 558 (1991).
- [3] Y. J. Lee, D. L. Feke, and I. Manas-Zloczower, *Chem. Eng. Sci.*, **48**, 3363 (1993).
- [4] J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970, Chapter 6.
- [5] H. Burrell, *Off. Dig.*, 726 (October 1955).
- [6] C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 2 (1968).
- [7] C. M. Hansen, *J. Paint Technol.*, **39**(505), 104 (1967).
- [8] C. M. Hansen, *Ibid.*, **39**(511), 505 (1967).
- [9] C. M. Hansen and A. Beerbower, in *Kirk-Othmer Encyclopedia of Chemical Technology* Suppl. Vol., 2nd ed. (A. Standen, Ed.), Wiley, New York, 1971, p. 869.
- [10] K. Shree, M. Yaseen, M. Ali, and P. Reddy, *J. Coatings Technol.*, **58**, 35 (1986).
- [11] K. V. S. N. Raju and M. Yaseen, *Langmuir*, **8**, 43 (1992).
- [12] H. C. Hamaker, *Phys.*, **4**(10), 1358 (1937).
- [13] F. M. Fowkes, *Ind. Eng. Chem.*, **56**(12), 40 (1964).
- [14] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978, Chapter 2.
- [15] W. B. Jensen, *The Relevance of Lewis Acid-Base Chemistry to Surface Interaction*, in *Surface and Colloid Science in Computer Technology* (K. L. Mittal, Ed.), Plenum, New York, 1987.
- [16] Y. J. Lee, D. L. Feke, and I. Manas-Zloczower, *Colloid Surf.*, **64**, 235 (1992).
- [17] F. M. Fowkes, following F. J. Mikale, Y. K. Lui, and A. C. Zettlemoyer, *Discuss. Faraday Soc.*, **42**, 238 (1966).
- [18] M. J. Marmo, M. A. Mostafa, H. Jinnai, F. M. Fowkes, and Y. A. Mason, *Ind. Eng. Chem., Prod. Res. Dev.*, **15**, 206 (1976).
- [19] M. E. Labib and R. Williams, *Colloid Polym. Sci.*, **264**, 533 (1986).
- [20] M. E. Labib and R. Williams, *J. Colloid Interface Sci.*, **97**(2), 356 (1984).
- [21] D. H. Solomon and D. G. Hawthorne, *Chemistry of Pigments and Fillers*, Wiley, New York, 1983, Chapter 2.
- [22] R. O. James and G. A. Parks, *Surf. Colloid Sci.*, **12**, 119 (1982).
- [23] Y. J. Lee, D. L. Feke, and I. Manas-Zloczower, *Powder Technol.*, **73**, 139 (1992).

- [24] A. F. M. Barton (Ed.), *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, Florida, 1983.
- [25] M. Arellano, Ph.D. Dissertation, Case Western Reserve University, 1995.
- [26] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York, 1987.
- [27] J. A. Dean (Ed.), *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985.
- [28] K. Raznjevic, *Handbook of Thermodynamic Tables and Charts*, McGraw-Hill, New York, 1976.
- [29] *CRC Handbook of Chemistry and Physics*, 70th Ed., CRC Press, Cleveland, Ohio, 1989.
- [30] Y. Marcus, *J. Solution Chem.*, 13(9), 559 (1984).
- [31] R. Schmidt, *Ibid.*, 12, 2 (1983).