
7 Methods of Characterization for Pigments, Fillers, and Fibers

Charles M. Hansen

ABSTRACT

Cohesion parameters for pigments, fillers, and fibers can often be evaluated by observation of the suspension and/or sedimentation behavior of particulate matter in different liquids. These characterizations are based on relatively stronger adsorption by some of the liquids compared with others. Those liquids with stronger interaction can suspend finer fractions of solids indefinitely or retard sedimentation, compared with the other liquids. Data should be interpreted by accounting for differences in the densities and viscosities of the test liquids, such that a relative sedimentation rate can be used for comparisons. The absolute sedimentation rates are generally not of primary interest. Data from such evaluations can be computer-processed to assign Hansen cohesion parameters (HSP) to the material in question. Cohesion parameter data are given for some newer pigments, fillers, and a carbon fiber to demonstrate the principles.

INTRODUCTION

The possibilities offered by cohesion parameter characterization of pigments, fillers, and fibers have not been generally recognized, judging from the relatively small number of publications appearing on the topic. Pigments and a few fillers were characterized in some of the author's first publications dealing with the solubility parameter.^{1,2} These were given δ_D , δ_P , and δ_H parameters (HSP) and a characteristic radius of interaction exactly analogous to the polymer characterizations discussed in Chapter 2 and Chapter 5. These data together with some more recent pigment characterizations are included in [Table 7.1](#), [Table 7.2A](#), and [Table 7.2B](#). Shareef et al.³ have also characterized pigment surfaces, including metal oxides. Gardon and Teas⁴ clearly showed the differences between zinc oxides treated and untreated with organic phosphate using a cohesion parameter characterization. Inorganic fibers have also been characterized.⁵ All of these characterizations again confirm the universality possible with these parameters. They reflect molecule–molecule interactions whether at surfaces or in bulk.

In the future, more systematic selection of dispersion aids should be possible, as these can also be described with the same energy parameters. Hansen and Beerbower have touched on this topic.⁶ Each segment of such molecules requires its own HSP. The discussion in Chapter 15 for the interactions within cell walls in wood demonstrates how this could be done. It has been shown by calculation that hemicelluloses act like surface-active agents, with some segments seeking lower-energy lignin regions and some segments (those with alcohol groups) orienting toward the higher-energy cellulose.

TABLE 7.1
HSP Correlations for Older Inorganic
Pigments^{1,2} and Metal Oxides³

Material	δ_D	δ_P	δ_H	Ro
Kronos® RN57 TiO ₂ ^a	24.1	14.9	19.4	17.2
Aluminum pulver lack 80 ^a	19.0	6.1	7.2	4.9
Red iron oxide ^a	20.7	12.3	14.3	11.5
Synthetic red iron oxide ^b	16.1	8.6	15.0	11.3
Synthetic yellow iron oxide ^b	17.3	6.0	14.5	12.5
Zinc oxide	16.1	8.6	15.0	11.3
	16.9	7.8	10.6	13.2
	16.2	10.8	12.7	9.8

Note: Units are MPa^{1/2}.

^a From Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient*, Doctoral dissertation, Danish Technical Press, Copenhagen, 1967. With permission.

^b From Shareef, K.M.A. et al., *J. Coat. Technol.*, 58(733), 35–44, February 1986. With permission.

METHODS TO CHARACTERIZE PIGMENT, FILLER, AND FIBER SURFACES

The cohesion parameter (HSP) approach to characterizing surfaces gained impetus by experiments where the suspension of fine particles in pigment powders was used to characterize 25 organic and inorganic pigment surfaces.^{1,2} Small amounts of the pigments are shaken in test tubes with a given volume of liquid (10 ml) of each of the test solvents, and then sedimentation or lack of the same is observed. When the solid has a lower density than the test liquid, it will float. Rates of floating have also been noted, but the term sedimentation will be retained here for both sedimentation and floating. The amounts of solid sample added to the liquids can vary depending on the sample in question, and some initial experimentation is usually advisable. If the pigment or filler particle size is large — say over 5 μm — the surface effects become less significant compared with a sample where the particle size is only 0.01 μm . Problems arise when the pigments are soluble enough to color the liquid such that sedimentation cannot be evaluated. The larger particle size pigments and fillers may sediment very rapidly.

Sedimentation rates have still been used successfully in some of these cases. The sedimentation rate is most easily expressed as the time at which the amount of particles, at a given point in the test tubes, has fallen to some small amount, perhaps zero. Observations can be made visually, or perhaps instrumentally, in a direction perpendicular to the incidence of a laser light. A visual observation is required in any event, as some samples seem to coat out rapidly on glass surfaces. Some pigments have portions that suspend for years in spite of large-density differences and relatively low-solvent viscosity. Satisfactory results from this type of measurement require some experience regarding what to look for. This can vary from sample to sample.

A characterization is less certain when there are only 4 or 5 good liquids out of the perhaps 40 to 45 tested, although this depends somewhat on which liquids are involved. “Good” in this context means suspension of particulates is prolonged significantly, compared with the other test solvents, after compensating for differences in density and viscosity. A corrected relative sedimentation time (RST) can be found by modifying the sedimentation time, t_s

TABLE 7.2A
List of Pigments Studied. HSP Results are Given in Table 7.2B

Pigment	Description
1.	TiO ₂ , Kronos RN 57, Titan Co. A/S., Frederikstad, Norway.
2.	Phthalocyanine Blue, B6, E. I. du Pont de Nemours and Co. (1949).
3.	Isolbonared Nr. 7522, C. I. Pigment Red 48 (C.I. 15865) (MnSalt), Køge Chemical Works, Køge, Denmark.
4.	Peerless Carbon Black
5.	Isol Fast Yellow IO GX 2505, C.I. Pigment Yellow 3, Køge Chemical Works, Køge, Denmark.
6.	Reflex Blau TBK Ext. (No C.I. Index-pigment mixture), Farbwerke Hoechst, Frankfurt (M), Germany.
7.	Isol Ruby BKS 7520, C.I. Pigment Red 57 (C.I. 15850) (Ca Salt), Køge Chemical Works, Køge, Denmark.
8.	Hansagelb 10 G, C.I. Pigment Yellow 3 (C.I. 11710), Farbwerke Hoechst, Frankfurt (M), Germany.
9.	Fanalrosa G Supra Pulver, Pigment Red 81 (C.I. 45160), BASF, Ludwigshafen, Germany.
10.	Heliogenblau B Pulver, C.I. Pigment Blue 15 (C.I. 74160), BASF, Ludwigshafen, Germany.
11.	Heliogengrün GN, C.I. Pigment Green 7, (C.I. 74260), BASF, Ludwigshafen, Germany.
12.	Permanentgelb H 10 G, C.I. Pigment Yellow 81, (No C.I. index), Farbwerke Hoechst, Frankfurt (M), Germany.
13.	Permanent Bordeaux FRR, C.I. Pigment Red 12 (C.I. 12385), Farbwerke Hoechst, Frankfurt (M), Germany.
14.	Permanent Violet RL Supra, C.I. Pigment Violet 23, (C.I. 12505), Farbwerke Hoechst, Frankfurt (M), Germany.
15.	Isol Benzidine Yellow G 2537, C.I. Pigment Yellow 12 (C.I. 21090), Køge Chemical Works, Køge, Denmark.
16.	Brillfast Sky Blue 3862, C.I. Pigment Blue 3 (C.I. 42140), J. W. and T. A. Smith Ltd., London.
17.	Permanent Orange G, C.I. Pigment Orange 13 (C.I. 21110), Farbwerke Hoechst, Frankfurt (M), Germany.
18.	Permanent Red, FGR Extra Pulver, C.I. Pigment Red 112, (C.I. 12370). Farbwerke Hoechst, Frankfurt (M), Germany.
19.	Isol Fast Red 2G 2516, C.I. Pigment Orange 5, (C.I. 12075), Køge Chemical Works, Køge, Denmark.
20.	Monolite Fast Blue 3 RS, Powder, C.I. Vat Blue 4 (C.I. 69801), Imperial Chemical Industries.
21.	Heliogenblau LG, Pulver, C.I. Pigment Blue 16 (C.I. 74100), BASF., Ludwigshafen, Germany.
22.	Red Iron Oxide.
23.	Carbon Black, Printex V (5519-1), Degussa, Frankfurt (M), Germany.
24.	Aluminum Pulver Lack 80, Eckart-Werke, 851 Fürth/Bayern, Germany.
25.	Isol Benzidine Yellow GA-PR, 9500, C.I. Pigment Yellow 12, Køge Chemical Works, Køge, Denmark.

Source: From Hansen, C.M., The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient, Doctoral dissertation, Danish Technical Press, Copenhagen, 1967. With permission.

$$RST = t_s(\rho_p - \rho_s)/\eta \quad (7.1)$$

ρ_p and ρ_s are densities of particle and test liquid, respectively, and η is the liquid viscosity.

A prolonged RST implies greater adsorption of the given solvent onto the surface in question. Characterizations based on these techniques tend to place emphasis on the nature of the surfaces for the smaller-particle-size fractions.

An example of a data sheet used for such studies is included in Table 7.3.

DISCUSSION — PIGMENTS, FILLERS, AND FIBERS

It can be reasoned that a pigment, filler, or fiber is most beneficial when the pigment surface and the binder in question have the same cohesion parameters. There are apparently no publications indicating a systematic modification of pigment surfaces to achieve a given set of cohesion parameters. The characterizations for some organic pigments are given in Table 7.4. These data indicate that their respective surfaces are essentially identical. An exception is the first one in the table where the analysis is based on only three good solvents that were able to extend sedimentation significantly relative to the other solvents tested.

TABLE 7.2B
Characteristic Parameters for Various Pigments Given in
Table 7.2A

Pigment	δ_t	δ_D	δ_P	δ_H	Ro	Comments
1.	16.8	11.8	7.3	9.5	8.4	Suspension
2.	10.5	9.3	3.1	3.7	2.3	Few suspending solvents
3.	10.0	8.7	3.5	3.5	2.5	Few suspending solvents
4.	13.6	10.3	6.0	6.6	6.0	Suspension
5.	11.9	10.2	4.8	3.8	4.4	Color only
6.	13.2	10.8	3.8	6.6	7.0	Mixed color and suspension
7.	10.5	9.6	3.0	3.2	3.9	Suspension
8.	10.5	9.1	4.0	3.3	3.3	Color only
9.	13.0	9.8	7.0	5.0	5.2	Color only
10.	12.0	10.8	3.5	4.0	5.2	Suspension
11.	12.0	10.0	4.8	4.5	4.8	Primarily suspension
12.	8.8	8.4	1.5	2.3	2.2	Suspension
13.	13.2	10.7	4.8	6.1	5.2	Color only
14.	11.5	9.6	5.2	3.6	4.4	Mixed color and suspension
15.	10.2	9.3	3.0	2.9	3.9	Mixed color and suspension
16.	13.3	9.5	7.2	6.0	5.1	Suspension
17.	11.5	9.7	3.9	4.7	4.5	Color only
18.	11.2	10.0	3.5	3.5	5.0	Color only
19.	14.2	10.9	5.6	7.1	7.0	Primarily color
20.	15.2	10.8	6.5	8.5	7.0	Suspension
21.	13.5	10.7	5.0	6.5	6.0	Suspension
22.	13.7	10.1	6.0	7.0	5.6	Suspension
23.	13.1	10.3	6.0	5.5	5.5	Suspension
24.	10.4	9.3	3.0	3.5	2.4	Suspension
25.	9.1	9.0	2.7	2.3	2.5	Suspension

Note: Units are (cal/cm³)^{1/2}.

Source: From Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient*, Doctoral dissertation, Danish Technical Press, Copenhagen, 1967. With permission.

These results suggest that pigment manufacturers have essentially arrived at the same result — a surface energy compatible with a wide variety of currently used binders. The solvents most frequently appearing as good for adsorption onto these surfaces include several chlorinated solvents, toluene, and tetrahydrofuran. As these solvents dissolve the most commonly used binders, one can conclude that the common binders will adsorb readily onto these pigment surfaces. This will give a good result, provided the solvent is not so good for the binder that it can remove the binder from the pigment surface.

Schröder⁷ (BASF) confirms that the optimum polymer adsorption will be found when the binder and pigment surface have the same HSP. He indicates that the solvent should be very poor for the pigment and located on the boundary region for the binder. He prefers the pigment to have HSP values placing it intermediate between the solvent and binder. This is suggested for conditions where the solvent has higher HSP than the pigment, as well as for conditions where the solvent has lower HSP than the pigment. This situation, with the solvent and binder on opposite sides of the pigment, means the composite vehicle has parameters very closely matching those of the pigment.

TABLE 7.3
Sedimentation Study

Solvent	D(Ds) 20°C	Viscosity 20°C	No.	D _p -D _s	Reference No.:			
					Sedimentation Time (min)		Relative Sedimentation Time (RST)	
					From	To	From	To
Acetone	0.79	0.35	4					
Acetophenone	1.03	1.90	6					
Benzene	0.88	0.65	13					
1-Butanol	0.81	4.00	28					
Butyl acetate	0.87	0.74	30					
Butyrolactone	1.29	1.92	37					
Carbon tetrachloride	1.59	0.99	40					
Chlorobenzene	1.10	0.80	41					
Chloroform	1.48	0.37	44					
Cyclohexane	0.78	1.00	47					
Cyclohexanol	0.95	68.00	48					
Diacetone alcohol	0.94	3.20	56					
<i>o</i> -Dichlorobenzene	1.31	1.27	61					
Diethylene glycol	1.12	35.70	75					
Diethyl ether	0.72	0.23	82					
Dimethyl formamide	0.95	0.82	90					
DMSO	1.10	1.98	94					
1,4-Dioxane	1.04	1.31	96					
Dipropylene glycol	1.03	107.0	98					
Ethanol	0.82	1.22	104					
Ethanolamine	0.91	24.10	105					
Ethyl acetate	0.89	0.44	106					
Ethylene dichloride	1.25	0.84	120					
Ethylene glycol	1.12	20.90	121					
Ethylene glycol monobutyl ether	0.90	2.90	123					
Ethylene glycol monoethyl ether	0.93	2.05	124					
Ethylene glycol monomethyl ether	0.96	1.72	126					
Formamide	1.13	3.30	131					
Hexane	0.66	0.33	140					
Isophorone	0.92	2.60	148					
Methanol	0.79	0.59	153					
Methylene dichloride	1.33	0.43	162					
Methyl isobutyl ketone	0.96	0.59	167					
Methyl-2-pyrrolidone	1.03	1.80	172					
Nitrobenzene	1.21	2.03	177					
Nitroethane	1.05	0.55	178					
Nitromethane	1.13	0.62	179					
2-Nitropropane	0.99	0.75	181					
Propylene carbonate	1.20	2.80	204					
Propylene glycol	1.04	56.00	205					
Tetrahydrofuran	0.89	0.55	222					
Toluene	0.87	0.59	225					
Trichloroethylene	1.47	0.58	229					

TABLE 7.4
HSP Correlations for Selected Materials

Material	δ_d	δ_p	δ_H	Ro	Fit	G/T
Organic Pigments						
Paliotol® Gelb L1820 BASF	18.9	3.5	10.5	5.4	0.99	3/35
Heliogen® Blau 6930L BASF	18.0	4.0	4.0	4.0	1.00	5/34
Socco Rosso L3855 BASF	17.3	5.7	2.7	4.1	0.99	4/34
Perm Rubin F6B Hoechst	16.7	3.7	3.1	4.8	0.88	6/33
Perm Gelb GRL02 Hoechst	16.7	2.5	3.7	4.5	0.95	5/37
Perm Lackrot LC Hoechst	19.0	5.0	5.0	4.0	1.00	7/28
Inorganic Pigments, Fillers, etc.						
Cabot Hochdisperse ^a	16.7	9.3	11.5	11.7	—	23/23
Cabot Hochdisperse	19.3	9.5	10.3	12.7	0.79	23/31
Zeta Potential Blanc Fixe ^b	26.5	19.1	14.5	20.4	0.95	5/19

Note: A perfect data fit of 1.0 means that there most probably are other sets of the same parameters that will have a data fit of 1.0 and also define a sphere that surrounds all the good solvents. A data fit of 0.99+ is preferred to define the optimum sphere for this reason. G/T is the number of good (G) liquids and the total (T) number of liquids in a correlation. Units are MPa^{1/2}.

^a Data analysis which only considers the good solvents to define the least sphere possible. See discussion of the SPHERE1 program in Chapter 1.

^b Data from Winkler, J., *Eur. Coat. J.*, 1–2/97, 38–42, 1997. With permission.

There is also a relation between how clearly a pigment can be characterized by sedimentation measurements and its zeta potential. Low zeta potential means sedimentation is rapid in all solvents, and this type of characterization becomes difficult or perhaps impossible. The zeta potential reflects the intensity (percentage coverage and number of layers) of the surface energy characteristics. It does not clearly indicate specific affinity relations of a given binder for the pigment surface, as a result of a given surface treatment, for example. This is given by HSP. To obtain a complete picture of the energetics of the surface, one needs an intensity factor, i.e., the zeta potential, as well as a qualitative factor, i.e., the cohesion energy parameters. The latter are generally lacking. One can suspect that some pigments have such high-intensity zeta potential — at some cost — that even though the cohesion parameters match poorly with a given binder, a system can still function satisfactorily. An HSP correlation for the zeta potential of blanc fixe is given in Table 7.4 using data from Winkler.⁸ This is discussed further in the following section.

Acid–base theories have been popular.^{9–11} The author has not found it necessary to resort to this type of approach in any activity, although many have clearly found them beneficial. More research is needed to fully understand the successes of the acid–base as well as the HSP approaches. It would seem that the HSP approach allows predictive ability that is not possible with an acid–base approach. However, the current problem is the lack of data.

Organic pigments normally have a good organic substrate on which to base an organic surface modification. The characterizations may reflect both a surface treatment and the surface of the base particles, depending on how the test liquids interact with these. It should not be too difficult to modify an organic surface to an alternative organic surface with satisfactory properties, if desired. It is conceptually and, in practice, more difficult to modify an inorganic surface to make it compatible with organic systems. This requires a significant change in surface energy from high to much lower and, presumably, also requires a greater degree of coverage to mask the base inorganic surface. The producers of inorganic pigments and fillers must either give their products suitable

surfaces, probably after much effort, or else one needs one or more supereffective additives to be able to achieve a good and stable dispersion. It helps to incorporate given (high-cohesion energy) groups in a grinding resin, such as acid, alcohol, amine, etc. The relatively high local cohesion parameters in the binder that are associated with these groups would indicate a high affinity for the high-cohesion-energy surface of the inorganic material. At the same time, these local regions of adsorbed polymer segments are not particularly soluble or are insoluble in the cheaper hydrocarbon solvents — for example, those that have much lower cohesion parameters. This provides a good, stable anchor on the pigment surface. The solvent will not dissolve that polymer or polymer segment away from the surface. Binders with high-acid numbers are frequently used, with success, in printing inks for the same reason. This is discussed in more detail in the following section.

It is felt that those who understand the use of cohesion parameters are able to more systematically modify surfaces of inorganic materials to optimize or improve their compatibility with organic polymers and binders. This has been done for inorganic Rockwool® fibers that are to be incorporated into polypropylene.⁵ It must be presumed that this type of systematic procedure can guide surface treatment of other inorganic materials in a more directed way toward a desired goal.

Data fits have been generally lower for characterizations of particulate solid surfaces, such as fillers, than for characterizations of polymers based on solubility. When testing is finished, the polymeric macromolecule is no longer a solid in the good solvents, whereas the particulate filler remains a solid. A macromolecule has various possibilities for contortions and the positioning of significant active groups in solution (or when swollen), giving a large number of possible (dynamic) structures that can be formed with the solvent. A rigid solid surface does not have this potential for adopting energetically desirable positions for its active groups. The adjustments for optimum local association must be made by the solvent molecules alone in the sedimentation testing. There are many solvents that do not retard sedimentation significantly, whereas the predictions based on the behavior of other solvents that do significantly retard sedimentation indicate that this should be the case. A contribution to the formation of the energetically desirable geometrical structures is not possible from the movement of rigid solid surfaces. Therefore, some solvents may not be able to retard sedimentation because they cannot adopt the geometrical positioning required to do this without the help of a mobile substrate. This lack of expected performance may be also partly due to solvent size, the location of the active groups, or combinations of these. These phenomena appear to be a significant area for future research.

HANSEN SOLUBILITY PARAMETER CORRELATION OF ZETA POTENTIAL FOR BLANC FIXE

Winkler⁸ has reported zeta potentials measured for 1% v/v blanc fixe with 0.34% moisture content. There were 19 liquids included in this careful study. These liquids could easily be divided into two groups. There were 5 systems with zeta potentials greater than about 10 mV and 14 systems with zeta potentials less than about 5 mV. Table 7.3 includes the results of the correlation of these data with cohesion parameters. The only major “error” was for hexamethylphosphoramide, with a RED of 0.951 and a zeta potential of 1.9 mV. This correlation supports the contention that cohesion parameters are significant for characterization of pigment, filler, and fiber surfaces. This is a good correlation and supports the views presented earlier. According to Winkler, there was no correlation with the acceptor or donor numbers (acid–base).

CARBON FIBER SURFACE CHARACTERIZATION

Hansen solubility parameters have been assigned to a carbon fiber surface, Panex 33 from Zoltek. After considerable refinement of the experimental technique, it was determined that two separate sets of HSP are required to describe the fiber surface. One of these sets has $\delta_D; \delta_P; \delta_H$ equal to

TABLE 7.5
HSP Correlations for Various “Carbon” Materials

Material	δ_D	δ_P	δ_H	R_o	Comments
Carbon fiber (high region) ^b	13.4	17.8	14.2	10.3	Sedimentation rate 3mm fibers
Carbon fiber (low region) ^b	17.2	3.4	2.0	3.9	Sedimentation rate 3mm fibers
Carbon black ^a	21.1	12.3	11.3	16.6	Suspension
Carbon black 1	17.9	8.1	8.9	6.2	Sedimentation (slow)
Carbon black 1 HT ^b	21.5	7.3	13.3	11.4	Sedimentation (rapid)
Carbon black 2 HT ^b	20.5	8.7	12.7	9.2	Sedimentation (rapid)
Carbon black 3 HT ^b	20.5	8.7	12.5	9.1	Sedimentation (rapid)
Carbon black 4 HT ^b	18.9	11.1	8.5	5.6	Sedimentation (rapid)
Petroleum coke	16.4	4.0	10.0	10.7	Sedimentation (slow)
Coal tar pitch	18.7	7.5	8.9	5.8	Solubility
C ₆₀ fullerene ^d	19.7	2.9	2.7	3.9	Solubility ^c

Note: Units are MPa^{1/2}.

^a Printex V (5519-1), Degussa

^b HT indicates a special heat treatment was performed prior to testing.

^c Log mole fraction solubility greater than -3.

^d Data from Hansen, C.M. and Smith, A.L., *Carbon*, 42(8-9), 1591-1597, 2004. With permission.

13.4;17.8;14.2, all in MPa^{1/2}. This corresponds to a highly polar surface with a significant hydrogen bonding component as well. The second set is characteristic of a hydrocarbon material with δ_D ; δ_P ; δ_H equal to 17.2;3.4;2.0, again in MPa^{1/2}. The hydrocarbon-like surface can be the backbone of the polyacrylonitrile (PAN) precursor for the fiber. Two separate sets of HSP assignments are confirmed by x-ray photoelectron spectroscopy (XPS) analysis. Two separate regions are found to coexist on the carbon fiber surface. The hydrogen bonding and polar contributions arise from the both bound and unbound (sizing/finish agent) chemical functionalities mainly in the form of hydroxyl, ether, carbonyl, carboxyl, amide, and nitrile groups. The carbonaceous backbone of the carbon fiber primarily accounts for the nonpolar region. This work was done as a part of the Framework program *Interface Design of Composite Materials* with the support of the Danish Research Agency, Ministry of Science, Technology and Innovation (STVF). The HSP characterizations were done at FORCE Technology, Broendby, Denmark, whereas the analyses were done at the Risø National Laboratory, Roskilde, Denmark.

Table 7.4 contains the HSP data used to construct Figure 7.1. These data confirm that “carbon” can be many things with widely different surface energies. The origins of the material, as well as the method in which it has been handled or treated, can completely dominate the nature of the surface of the given materials and their solubility, if this is possible.

CONTROLLED ADSORPTION (SELF-ASSEMBLY)

Significant tasks for formulators are to control the surface and interfacial energies of products, especially if they are water reducible. This is required to allow substrate wetting, to maintain stable dispersions, and to provide/ensure adequate and durable adhesion to given substrates. Guidelines for courses of action are frequently available when cohesion energy parameters are referred to. Some guides are discussed in the following.

It is a well-known fact that a small percentage of acid groups (or alcohol groups) on a polymer chain will promote adhesion and adsorption to many surfaces. The cohesion energy parameter of an isolated acid group is high. One can consider the cohesion energy properties of formic acid (δ_D ;

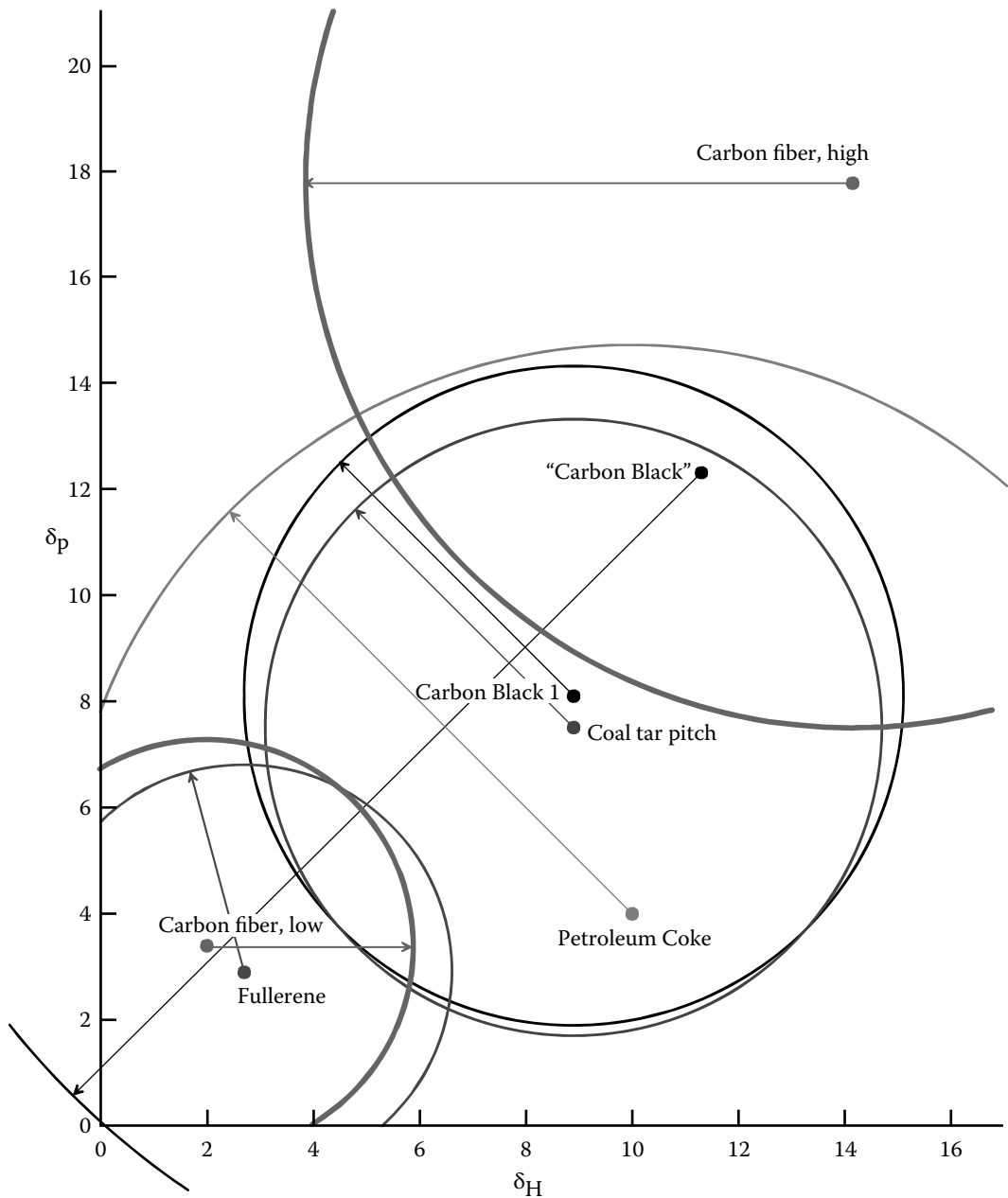


FIGURE 7.1 Characterization of a carbon fiber and comparisons of this with other carbon materials. Units are $\text{MPa}^{1/2}$. The work on which this figure is based was supported by the Framework program *Interface Design of Composite Materials* (STVF fund No. 26-03-0160). Reproduced with permission.

δ_p ; $\delta_H = 14.3$; 11.9 ; 16.6) as an isolated part of a polymer chain. The polar cohesion energy parameter of an acid group is not so high. It would seem logical to systematically use acid groups for adsorption to high-energy surfaces and to make certain that the cohesion energy parameters for the solvent and bulk of the product are much lower, such that isolated acid groups would not be dissolved. This would provide an anchor that the product will not be able to remove. This type of adsorption may be called *hydrophilic bonding*. If, on the other hand, the solvent were too good for the anchor,

it could be presumed that even an acid group may be too readily dissolved off the surface or at least take part in a dynamic equilibrium of adsorption and desorption. Absorbed/adsorbed water can sometimes interfere with such anchors at high-energy surfaces.

The reverse of this thinking is systematically used by those designing associative thickeners and also by nature, such as the hydrophobic bonding in proteins. Certain segments of given molecules have such low cohesive energy parameters that they are no longer soluble in the media, which is usually aqueous, and they either seek out their own kind (associate) or perhaps adsorb on or penetrate into a low-energy surface where cohesion energy parameters more suitably match. The positive effects of associative thickeners can be counteracted by the presence of solvents preferentially locating where the hydrophobic bonding is to occur. The hydrophobic bonds lose strength or may even dissolve away.

A challenge to the creative mind is to derive new uses for high-energy groups that are not particularly water soluble or sensitive. The division of the cohesion energy into at least three parts allows these considerations to be made in a reasonably quantitative manner. One can choose nitro groups or perhaps groups containing phosphorus as examples of species characterized by high-polar-cohesion-energy parameters and low or moderate hydrogen bonding parameters. The total cohesion energy parameters for ethanol and nitromethane are very close: 26.1 and 25.1 MPa^{1/2}, respectively. Ethanol is soluble in water, nitromethane is not. Ethanol has a relatively high-hydrogen bonding parameter (19.4 MPa^{1/2}) compared with nitromethane (5.1 MPa^{1/2}). This makes all the difference. Would not the nitro group be a suitable anchor analogous to the previous discussion concerning acid groups? Also, it would not be hydrophilic with the inherent problems of water sensitivity associated with high-hydrogen bonding parameters. Several of the pigments reported in [Table 7.4](#) did indeed have moderate affinity for the nitroparaffins, for example, but they were included in the lesser interacting group by the arbitrary division into good and bad groups.

CONCLUSION

Many pigments and fillers have now been characterized by Hansen cohesion parameters (HSP). Many examples are given. A method based on relative sedimentation time and/or suspension is described for doing this. This method has generally allowed useful characterizations, although some experience is helpful. For example, the data are often scattered and not nearly of the quality usually found when observing polymer solution behavior. This scatter of data for untreated surfaces in particular may cause some to disregard the method; hopefully, they can develop a better one. The obvious advantages of having solvents, plasticizers, polymers, pigments, fillers, fibers, etc., characterized with the same energy parameters should provide incentive for improving on the present state, both in terms of numbers of characterizations as well as improved methodology. One assumes that maximum physical adsorption is accompanied by closely matching HSP. Local adsorption by so-called active groups (alcohol, acid, amine) having the required match, can give anchors on a surface that may no longer be soluble in the continuous media, and therefore will remain in place as required.

REFERENCES

1. Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient*, Doctoral dissertation, Danish Technical Press, Copenhagen, 1967.
2. Hansen, C.M., *The three dimensional solubility parameter — key to paint component affinities II. J. Paint Technol.*, 39(511), 505–510, 1967.
3. Shareef, K.M.A., Yaseen, M., Mahmood Ali, M., and Reddy, P.J., *J. Coat. Technol.*, 58(733), 35–44, February 1986.

4. Gardon, J.L. and Teas, J.P., Solubility parameters, in *Treatise on Coatings, Vol. 2, Characterization of Coatings: Physical Techniques*, Part II, Myers, R.R. and Long, J.S., Eds., Marcel Dekker, New York, 1976, chap. 8.
5. Hennissen, L., Systematic Modification of Filler/Fibre Surfaces to Achieve Maximum Compatibility with Matrix Polymers, Lecture for the Danish Society for Polymer Technology, Copenhagen, February 10, 1996.
6. Hansen, C.M. and Beerbower, A., Solubility parameters, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., 2nd ed., Standen, A., Ed., Interscience, New York, 1971, pp. 889–910.
7. Schröder, J., Colloid chemistry aids to formulating inks and paints, *Eur. Coat. J.*, 5/98, 334–340, 1998.
8. Winkler, J., Zeta potential of pigments and fillers, *Eur. Coat. J.*, 1–2/97, 38–42, 1997.
9. Vinther, A., Application of the concepts solubility parameter and pigment charge, *Chim. Peint. (England)*, 34(10), 363–372, 1971.
10. Soerensen, P., Application of the acid/base concept describing the interaction between pigments, binders, and solvents, *J. Paint Technol.*, 47(602), 31–39, 1975.
11. Soerensen, P., Cohesion parameters used to formulate coatings (Kohaesionsparametre anvendt til formulering af farver og lak), *Färg och Lack Scand.*, 34(4), 81–93, 1988 (in Danish).
12. Hansen, C.M. and Smith, A.L., Using Hansen solubility parameters to correlate solubility of C₆₀ fullerene in organic solvents and in polymers, *Carbon*, 42(8–9), 1591–1597, 2004.