Polymer additives and solubility parameters

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Abstract

The solid and liquid additives used in polymers can be characterized by Hansen solubility parameters (HSP). Compatibility is found when these parameters for the polymer and the additive are close enough to each other. Mismatches lead to phase separation, or in the case of solid surfaces, to poorer adhesion than that otherwise attainable. Where the additives have distinctly different segments, such as surface-active agents, the respective segments seek regions of similar energy (HSP). Some additional information is included in [2].
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1. Background

Additives used in polymers can be characterized by Hansen solubility parameters (HSP), just like polymers. These usually have the symbols δ_D, δ_P, and δ_H, which are sometimes replaced by D, P, and H, for convenience. The assignment of HSP to both additives and the polymers to which they are added allows predictions of behavior that can improve performance, insure stability, reduce costs, and maintain or improve environmental acceptability.

The background for the HSP is found in detail in [1]. Briefly, the basis of these parameters is a division of the cohesion energy of volatile liquids into three parts. When a liquid evaporates all the bonds holding it together are broken. The three Hansen solubility parameters quantitatively represent the nonpolar (atomic) bonding, the permanent dipole-permanent dipole (molecular) bonding, and the hydrogen (molecular) bonding. The methods used to achieve this division have been confirmed experimentally. Where experimental data is lacking, group contribution methods can be used as a first estimate of the behavior of the untested mate-

rials. Reference [1] contains over 400 HSP correlations for polymers and pigments and over 850 HSP values for gases, liquids, and low molecular weight solids. This latter number has been increased to over 1200 in the author's unpublished database.

The RED number (relative energy difference), which is calculated from the difference in HSP between the materials involved, is frequently used as a single parameter to evaluate the compatibility relations of the two materials. This parameter (described in [1] and in the appendix to [2]) simplifies comparisons because it is 0 for a perfect match in the HSP of the two materials. The RED number is 1.0 at the limit of compatibility. RED numbers less than 1.0 indicate compatibility, while progressively higher RED numbers indicate progressively less compatibility. One can also generate HSP correlations based on some given amount of swelling or uptake rather than complete solubility, in which case RED equal to one indicates compatibility at the amount used to separate the "good" solvents from the "bad" ones.

Nonvolatile materials such as polymers and pigments can be assigned HSP by analysis of their interactions with a set of well-defined liquids. As stated above, hundreds of polymers and pigments have been assigned these parameters. Many additives used in polymers have also been characterized, but a

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major characterization activity is required before completely systematic use of HSP in this area is possible.

2. Solubility

Solubility plays an important role in the behavior of many additives. If full compatibility is required, then full solubility is mandatory. Limited solubility of the additive in a given polymer may also be acceptable, but limited solubility can also lead to problems.

Temperature effects can become very important when the amount of additive in a polymer is close to the solubility limit at the temperature of use. Many problems have arisen because of additives with limited solubility in a given polymer, for example. At elevated temperatures the solubility of such an additive is increased. If there is a rapid cooling, the polymer becomes supersaturated. That portion of the additive that dissolves at the higher temperature, and which is no longer soluble at the lower temperature, has been known to migrate to an air surface and to appear there as a dust-like material for solids, or as an oil in the case of liquids. This can happen for colored organic pigments and can occur for other types of additives as well. Pigments that tend to "bleed", for example, are prone to this phenomenon. The author experienced a related phenomenon where a UV-absorber was soluble in a liquid coating, but not in the dried film. It appeared at the air surface as a white powder.

Solubility relations can be systematically explored both for an additive and for a polymer (system) in question. The physical situation can be clarified, and in many cases a formulating solution can be found. When HSP data are lacking these can sometimes be satisfactorily estimated by calculation, but it is most often preferred to experimentally determine the solubility of the materials involved in a series of well-chosen liquids. Solution or not at the 10% level is often used to find the "good" and "bad" solvents. The HSP of the solute can be found by similarity to the good solvents. A computer program can be used for this purpose. Compatibilizing steps can then be systematically taken. These may include modifying one of the materials or adding/removing a well-chosen material.

In some cases the additives must be present at least to some minimum amount in order to function effectively. UV-stabilizers, antioxidants, and the like belong to this group. If the HSP are known for a series of these additives, then one can quickly determine which are most soluble in a given polymer. To my knowledge, this information is not available. It should be noted that additives will be located in the amorphous regions for partly crystalline polymers. There will be no transport through crystalline regions.

Masterbatches (most) often contain polymers as stabilizers that are different from the polymers into which they are incorporated. The compatibility of these polymers can be quite critical in given situations. Methods to improve compatibility can be systematically found using HSP.
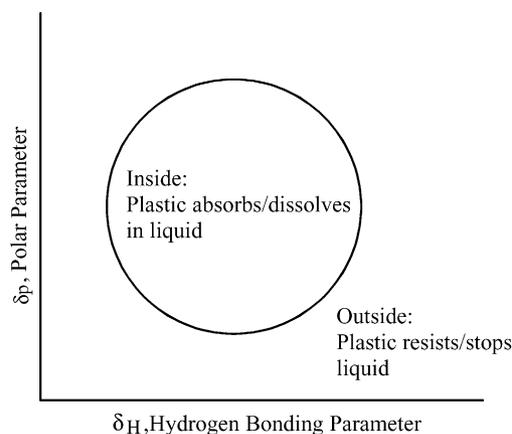

Fig. 1. Hansen solubility parameter diagram.

Table 1
HSP for some materials of interest in connection with di(2-ethylhexyl phthalate)

Material	D	P	H	V
Di(2-ethylhexyl phthalate) (DEHP)	16.6	7.0	3.1	377.0
2-Ethylhexyl phthalate (MEHP)	17.3	6.2	6.8	265.0
Dioctyl adipate (DOA)	16.7	2.0	5.1	400.0
Di(isononyl phthalate) (DiNP)	16.6	6.6	2.9	432.4

The units of D, P, and H are MPa$^{1/2}$, and that of V is cm^3/mole.

3. Plasticizers

Many plasticizers have been characterized by HSP and their general behavior with regard to solubility and compatibility follows that of the solvents. Some differences are encountered due to generally higher molecular weights. This means lowered compatibility in boundary situations, and slower transport (diffusion) through polymer matrices. The general behavior can be interpreted from the sketch in Fig. 1. There is a circular (spherical for three dimensions) region indicating complete compatibility with the polymer when the given HSP for the plasticizer indicate a position well within the circle. Marginal compatibility is found for a plasticizer near the boundary of the circle, and incompatible situations will be found when there is a greater mismatch in the HSP of the polymer and plasticizer. There are possibilities for synergistic mixtures when two plasticizers are mixed, and when the mixture has HSP closer to the HSP for the polymer (Table 1).

4. Fire retardants

In terms of compatibility, the liquid fire retardants will behave in a manner similar to the plasticizers, and the solid fire retardants will behave in a manner similar to the pigments and fibers (see below).

A special concern exists for the brominated fire retardants in that their spreading in the environment is not desired. The brominated fire retardants (BFR) have HSP which strongly

Table 2
The affinities of tetrabromobisphenol A (TBBPA) for selected biological materials (units are MPa$^{1/2}$)

Material/correlation	D	P	H	Radius	Dist. TBBPA
TBBPA	20.2	9.1	13.8	–	0.0
Pentachlorophenol	21.5	6.9	12.8	–	3.5
Lignin solubility correlation (RED = 0.50)	21.9	14.1	16.9	13.7	6.8
Rapid skin permeability correlation (RED = 1.36)	17.6	12.5	11.0	5.0	6.5
Swelling of psoriasis scales correl (RED = 0.49)	24.6	11.9	12.9	19.0	9.3

All data are found in [1] except for those for TBBPA that are estimated by group contributions.

suggest that they will follow the same routes as chlorinated materials with reasonably similar HSP. The data in Table 2 confirm that the expected physical behavior of a typical BFR (TBBPA, tetrabromobisphenol A) will resemble that of pentachlorophenol. It readily absorbs into the outer layer of human skin, which is very well modeled by psoriasis scales, with reasonably rapid further skin penetration, dictated mostly by the size of the molecule. It will also readily dissolve into wood (lignin).

TBBPA has a distance from pentachlorophenol (PCP) of only 3.5 units. This is very close and means that where PCP is soluble, TBBPA will also be soluble.

TBBPA has a distance from the center of the spherical HSP correlation for Lignin solubility of only 6.8 units. Dividing this by the radius of the sphere to find the RED number (relative energy difference) shows that it is well within the solubility region with a RED of 0.5. TBBPA is readily soluble in lignin (wood).

TBBPA has a distance from the center of the spherical correlation for rapid skin permeation of 6.5. This is just outside the region for rapid permeation, but means that permeation will certainly take place at a moderate rate. The size and shape of the molecule will dictate the rate of permeation, not the solubility relations.

TBBPA will readily absorb into the outer layer of the skin (keratin) here described by swelling of psoriasis scales. The rate of absorption is dictated by the size and shape of the molecule, and not by the solubility relations.

5. Heat and light stabilizers

Heat and light stabilizers can also be assigned HSP. These values will indicate compatibility relations in given polymers. It is known that many additives can migrate from one polymeric material, coating, or layer into another. This is only possible when the match between the HSP for the additive and the given polymer are suitably close. The rate of migration depends on the local diffusion coefficient. In most cases this diffusion coefficient can be expected to be concentration dependent, that is, to increase with increased concentration of the additive. As stated above, it should be noted that no transport will occur through crystalline regions. The additives will be located in the amorphous regions, and remain in these.

6. Antistatic agents

Antistatic agents must be present at the air/plastic surface in order to function properly. This usually requires some degree of incompatibility with the polymer in question, and most probably a lower surface tension than that of the polymer. Sometimes only one part of the additive molecule has a lower surface tension. An example is glycerol monostearate, a common antistatic agent for polyolefins. The stearate portion is compatible in amorphous polyolefin regions and has a low surface tension keeping some of it at the air surface. The two remaining alcohol groups can collect water when they are at the polymer/air surface. The increased amount of water in the surface increases electrical conductivity, and less dust is collected since static electricity does not build up. The general criteria for antistatic agents are therefore some segment allowing marginal compatibility with the polymer and some segment that collects water. The former segment will generally have low HSP and the latter will generally have high HSP.

7. Pigments and fibers

HSP are derived from bulk energies through the latent energy of vaporization. There are numerous correlations of HSP and surface phenomena including the surface tension (surface free energy) of liquids and polymers [1]. When dealing with surfaces it is more appropriate to use the terminology cohesion parameters instead of solubility parameters, but HSP will be used here for both. These are numerically identical. Many surfaces, including those of pigments, fillers, and fibers, can be experimentally characterized by HSP. The HSP of the test material can be found from the HSP of those liquids with the strongest interaction. This allows predictions of interactions with all of the other materials whose HSP are known.

HSP characterizations are highly recommended when the value of a product can be markedly enhanced by systematic and careful formulation to optimum conditions. Surfaces with larger areas, such as substrates for paint, printing ink, adhesives, etc., can be characterized by HSP by observing how droplets of well-chosen liquids behave. Those liquids that spontaneously spread either have high affinity for the surface, or else they have significantly lower surface tension

Table 3
Hansen cohesion parameter correlations for selected solids

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	0.945	5/37
Perm Lackrot LC Hoechst	19.0	5.0	5.0	4.0	1.00	7/28
Inorganic pigments, fillers, etc.						
Kronos RN57 TiO_2	24.1	14.9	19.4	17.2	[a]	[a]
Aluminum Pulver Lack 80	19.0	6.1	7.2	4.9	[a]	[a]
Red Iron Oxide	20.7	12.3	14.3	11.5	[a]	[a]
Cabot Hochdisperse[b]	16.7	9.3	11.5	11.7	–	23/23
Cabot Hochdisperse	19.3	9.5	10.3	12.7	0.788	23/31
Zeta Pot. Blanc Fixe	26.5	19.1	14.5	20.0	0.948	5/19

The HSP and Ro are in units of $MPa^{1/2}$. The FIT should be 1.000 for all good solvents (*G*) out of a total number of test liquids (*T*) having Ra less than Ro.

[a] Not available, not recorded at time of study.
[b] Special technique where the "sphere" encompasses all good solvents.

than the surface. Getting good numbers for HSP in this type of study is problematic because of the latter phenomena.

Solid materials can be characterized in powder form (pigments, fillers, fibers) by sedimentation rates in a set of well-chosen liquids. A normalization of the sedimentation rate for viscosity and density differences allows direct comparison of a relative sedimentation rate among the different solvents. Those solvents with longest relative sedimentation rates are those that adsorb onto or disperse the powders best, and therefore have energy properties closest to those of the surface of the powder in question. Details of this procedure are described in [1]. Pigments, fillers, solid additives of various types, and fibers in plastics will have better physical adhesion to the matrix polymer when their HSP (surface) values match closely with the HSP of the polymer (or special segments thereof) (Table 3).

8. Other additives

Surfactants, adhesion promoters, dispersion aids, and the like have a general requirement that there must be affinity to two distinct phases. This implies molecules having segments with HSP "similar" to the HSP of those phases where they are intended to locate. The use of "similar" is because the degree of desired match may vary widely from system to system. In coatings, for example, it is well known that acid and alcohol groups on a polymer molecule will improve ease of dispersion and dispersion stability since these groups adsorb readily onto the surface of most inorganic surfaces, in particular. The high energy (high hydrogen bonding parameter) of these groups matches the correspondingly high hydrogen bonding parameter of the given surfaces. Once this high-energy anchor has

Table 4
Hansen solubility parameters for selected chemicals (units are $MPa^{1/2}$)

Chemical	δ_D	δ_P	δ_H	Molar volume
Amphetamine	17.5	4.3	6.3	148.1
Bisphenol A	19.2	5.9	13.8	207.5
D-Camphor	17.8	9.4	4.7	153.7
2-Ethyl hexyl phthalate				
MEHP	17.3	6.2	6.8	265.0
Hexanal	15.8	8.5	5.4	120.2
Nicotine	18.5	7.8	6.5	160.7
L-Menthol	16.6	4.7	10.6	175.6
Paracetemol	17.8	10.5	13.9	151.2
Paraquat	19.5	8.8	5.9	186.0
Skatole	20.0	7.1	6.2	122.6
2-Tert-butyl-4-methyl phenol	17.3	3.7	10.5	177.6
Triacetin	16.5	4.5	9.1	188.2
Triclosan	20.0	7.7	10.0	263.0
Vanillin	18.6	10.6	13.8	144.1
Ecstacy*	18.0	5.2	6.3	181.0
Serotonin*	18.0	7.4	13.0	176.2
Dopamine*	18.2	9.0	17.1	153.0
Adrenaline*	20.5	8.0	18.3	183.0
Saccarine*	21.0	13.4	8.5	221.2
Caffeine*	19.5	10.1	13.0	157.9
Quinine*	19.0	4.4	10.5	324.4
Spermidin*	16.7	11.2	12.0	152.6
Meclofenoxate*	16.0	6.4	9.3	185.5
Norephedrin*	18.0	8.3	18.7	183.0
Ascorbic acid*	18.0	9.8	21.6	176.1

These values are calculated or estimated with the techniques described in [1]. The units for the molar volume are cc/mole. The compounds indicated with an (*) are based on an assumed density of 1.0 g/cc. To the extent this is in error, adjustments will be necessary to δ_P, δ_H, and the molar volume. δ_D is estimated by similarity to related compounds and requires no correction for this reason.

been established it is not readily disturbed by the other components of most polymer-based systems, since HSP of the bulk of the components is too low.

Table 4 is included to show that a wide variety of materials can be assigned HSP.

9. Conclusion

Polymer additives can be assigned Hansen solubility parameters (HSP). Potential predictions of the physical behavior of polymeric additives in polymers are therefore possible. This allows systematic studies of compatibility, surface affinities, and the like to improve the performance of the coatings and plastics containing these additives.

References

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[2] C.M. Hansen, Aspects of solubility, surfaces and diffusion in polymers, Prog. Org. Coat. 51 (2004) 55–67.