A Primer on Perfuming Polymers

By Martin Meder, Hightstown, New Jersey

The ability to predict which fragrance chemicals can solvate in what polymers is important for several reasons. It saves development time by eliminating obvious dead ends from consideration at the start. It allows the incorporation of larger amounts of fragrance than would otherwise be possible; up to 30-50% of a polymer can be fragrance. It avoids phase separation problems ranging from foggy dispersions of perfume droplets in supposedly clear polymers to outright immiscibility. Finally, it assures that fragrance materials that are intended to soak into fibers or films for slow release actually do so, rather than just sit on the surface.

Of course, the term "polymers" encompasses not only those materials commonly thought of as being made of "plastic," but also paper, leather, wood, adhesives, natural and synthetic fabrics.

This primer will attempt to cover, as painlessly as possible, some basic polymer physics and solubility theory and then show how this knowledge can be applied in general and for a specific example.
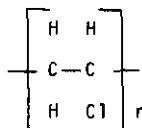
Background

A polymer may be thought of as a chain of many identical, connected links called, to no one's surprise, "mers." These are used to represent the polymer as shown for poly(vinylchloride) in figure 1.

The subscript, n, is often seen; it is the average number of links in the chain and is called the "degree of polymerization." If the chains comprising a given polymer are randomly arranged, like cooked spaghetti, then the polymer is called "amorphous." If the polymer has ordered regions where the chains are lined up, like spaghetti in the box, then the polymer is called "crystalline." In reality these are crystalline-amorphous because there are no commercial 100% crystalline polymers, although some are 90% crystalline.

Crystals have melting temperatures where they change from ordered solids to disordered liquids, but what about amorphous polymers which are already disordered? These are supercooled liquids similar to window glass that are characterized by their "glass transition temperature (Tg)." An amorphous polymer that is at a temperature below its Tg is hard, brittle and glass-like. However, if it is at a temperature above its Tg, then it is soft, tough and more plastic (read: formable). Very simply, when an amorphous polymer is heated through its Tg, the thermal vibrations of the chains become large enough to overcome the forces of attraction holding the chains to each other. When this happens, the chains are free to slide over each other, and the bulk polymer can be bent without breaking. There is another way to accomplish this freedom of motion.

Figure 1. Poly(vinylchloride), commonly known as PVC or "Vinyl"

Plasticizers

The Tg of a polymer can be lowered by introducing a lubricant between the chains (adding sauce to the spaghetti). For instance, the Tg of PVC is normally 85°C, it is rigid and glassy when it is at a temperature below this. The addition of 30% dioctyl adipate (a lubricant) reduces the Tg to below −40°C so that at room temperature it is flexible and plastic. These lubricants are properly called "plasticizers." Good plasticizers have these qualities:

- high boiling points to minimize volatilization and to survive processing.
- high molecular weights to slow diffusion losses from the bulk of the polymer.
- as low in color as possible.
- as low in odor as possible.
- most importantly, very soluble in the polymer.

It will be seen shortly that, except for odor quality, fragrance chemicals can meet these requirements and substitute for all or part of the plasticizer found in a polymer.

Solubility

How can it be determined, a priori, that a given chemical will be a good solvent for a polymer? One way to think about the problem is to consider a polymer where the chains are tightly attracted to each other in a solvent whose molecules are only loosely attracted to each other. In this case, the solvent molecules cannot squeeze between the polymer chains and the polymer does not dissolve. Since solvation is mutual and the polymer must dissolve the solvent as well, we must consider the converse: if the solvent molecules are strongly attracted to each other then polymer chains which are weakly bound to themselves will be unable to fit between the solvent molecules and solvation will not occur. Therefore, for optimum solubility, the forces of attraction that hold together the polymer and the solvent should be as close to each other as possible. When this is the case, simple entropy of mixing will supply the driving energy for solvation.

Maximum utility of this information is only possible if the forces of attraction can be quantified. It seems reasonable that solvents that require more energy to evaporate them at room temperature (ΔE) would have greater attractive forces holding them together. Also, it can be expected that in a solvent with higher attractive forces, a given number of the molecules will occupy a smaller volume than would be the case in a solvent with low attraction between molecules. This is called the molar volume (V) and it is the molecular weight in grams (MW) divided by the density (ρ) in grams per cubic centimeter. One possible measure then of these forces of attraction would be $\Delta E/V$. In fact this term is known as the "cohesive energy density." A much more commonly encountered term is the square root of this quantity, known as the solubility parameter, δ:

$$\delta = (\Delta E/V)^{1/2}$$

where the units of the solubility parameter, δ, are in Megapascals$^{1/2}$ in the SI system (1 MPa$^{1/2}$ = 1 J$^{1/2}$cm$^{-3/2}$ = 0.48888 cal$^{1/2}$cm$^{-3/2}$). A more rigorous derivation is given in reference 1.

As a rule of thumb, a solvent and a polymer should be within 2 MPa$^{1/2}$ to assure compatibility. While large compilations of solubility parameters exist for both common solvents and polymers,[2] the energies of vaporization of fragrance chemicals are hard to come by, as can well be imagined. Fortunately, the solubility parameter can be calculated in several ways. One of these relies on an empirical correlation between the heat of vaporization at room temperature and the boiling temperature (T_b), developed by Hildebrand and Scott:[3]

$$\Delta E = 18{,}578 + 144.9 T_b + 0.0837(T_b)^2$$

This equation is adapted in that it yields energy rather than heat of evaporation, it is in SI units, and T_b is in degrees centigrade. This equation is fine for poor hydrogen bonding, non-polar solvents like pinene, but requires the addition of correction factors for moderate and strongly hydrogen bonding solvents. These were developed by Burrell[4] and are added to the results of calculating the solubility parameter:

Add 2.9 MPa$^{1/2}$ for alcohols

Add 1.2 MPa$^{1/2}$ for esters

Add 1.0 MPa$^{1/2}$ for ketones with T_b less than 100°C, otherwise add nothing

Unfortunately the correction factor for aldehydes appears not to have been developed, but there is another way to determine the solubility parameter, as will be seen.

The hydrogen bonding mentioned earlier will also have an influence on miscibility. The degree of hydrogen bonding in the solvent should match that of the polymer. Hydrocarbons are poor hydrogen bonders while ethers, ketones and esters are moderate and alcohols, acids, amides, amines and aldehydes are strongly hydrogen bonding.

PVC, An Example in Detail

Poly(vinylchloride) is an extremely important polymer for several reasons. It is second only to poly(ethylene) in tonnage sold. Unlike poly(ethylene), it is almost always compounded with a plasticizer. This is important because it means that a fragrance can be added at the same time with no additional processing.

Other reasons for its importance are evident. At this writing, bulk PVC is less than $0.40 per pound. PVC is processed with a greater variety of techniques, into a greater variety of products, than any other polymer. The U.S. and Canadian vinyl compounding capacity is 1.35 million metric tons per year. If 10% of this were perfumed at the 1% level it would mean sales of 1,350 tons of fragrance per year. Finally, the physical properties of PVC lend themselves very well to accepting fragrance chemicals.

PVC is a moderately hydrogen bonding polymer with a solubility parameter of 19.4 MPa$^{1/2}$ and encounters processing temperatures on the order of 177°C. Additionally, it is an acidic polymer in the Lewis sense. The chlorine atoms act to withdraw electrons from adjacent hydrogen atoms on the chain, giving them a positive sense. These then can attract electron pair donors (Lewis bases) such as the carbonyl oxygens of esters and ketones as well as ether oxygen. This behavior is very important[5] because the acid-base neutralization contributes a heat of mixing which further assures rapid solvation.

A data base was created for materials with reported boiling points at atmospheric pressure using the empirical equation presented earlier. Even though plasticizers are usually liquid at room temperature, solids with densities reported for their liquid phase at slightly above room temperature were included, recognizing, of course, that any real polymer perfume would be a mixture that would likely depress the melting point of any solid component to below room temperature. This data base was then sorted to contain only moderately hydrogen bonded Lewis bases with boiling points above 177°C. The results are presented in order of increasing solubility parameter in Table I.

Recalling that compatibility can be expected when the solubility parameter of the plasticizer is within 2 MPa$^{1/2}$ of the plastic's solubility parameter, the range for PVC is then 17.4 to 21.4. Looking at Table I, this is obviously as fortuitous a coincidence as could be hoped for.

But what about evaluating candidates that are not on the list, such as those with boiling points too high to be measured at atmospheric pressure? A slightly more involved technique called the "group addition method" may be used. In this method, the solubility parameter is determined by summing the contribution toward the solubility parameter of each of the chemical groups (its group value, G) on the molecule and then dividing by the molar volume:

$$\delta = \frac{276.3 + \Sigma G}{V}$$

The group values, G, for the various groups are given in Table II.[6] An example will help. Ethylene brassylate has a molecular weight of 270.37 g/mole, a density of 1.04 g/cc and a structure that looks like figure 2. The molar volume is 270.37 g/mole/1.04 g/cc or V = 259.97 cc/mole. There are 13 methylene groups worth 269.0 each or 3,497.0. There are 2 ester groups worth 668.1 or 1,336.2. The solubility parameter is then:

$$\delta = \frac{276.3 + 3497.0 + 1,336.2}{259.97}$$

$$\delta = 19.7 \, MPa^{1/2}$$

This is an ideal material for compounding with PVC.

Table I. Candidates for Perfuming PVC

Name	S(MPa$^{1/2}$)	T$_b$ °C	MW (g/mole)	S (g/cc)	V (cc/mole)
2-Undecanone	16.6	232.0	170.29	0.8261	206.13
Ethyl laurate	16.7	269.0	228.36	0.8670	263.39
Isoamyl isovalerate	16.9	193.0	172.26	0.8580	200.76
2-Nonanone	17.0	195.3	142.23	0.8188	173.70
Linalyl acetate	17.0	220.0	196.28	0.8950	219.30
1-Octen-3-yl acetate	17.1	190.0	170.24	0.8730	195.00
Octyl acetate	17.2	199.0	172.26	0.8730	197.31
Phenyl methyl carbinyl propionate	17.2	226.0	220.24	1.0130	217.41
Isoamyl butyrate	17.3	179.0	158.23	0.8660	182.71
Menthyl acetate	17.3	227.0	198.30	0.9190	215.77
Menthone	17.4	210.0	154.24	0.8895	173.40
Phenyl methyl carbinyl acetate	17.4	212.0	206.24	1.0291	200.40
Terpinyl acetate	17.5	220.0	196.28	0.9570	205.09
Thujone	17.5	201.0	152.23	0.9120	166.91
Ethyl caprylate	17.6	209.0	172.26	0.8780	196.19
Fenchone	17.6	193.0	152.23	0.9501	160.22
Geranyl acetate	17.7	245.0	196.28	0.9080	216.16
Bornyl acetate	17.8	226.0	196.28	0.9772	200.85
Pulegone	18.4	223.0	152.23	0.9372	162.43
p-Cresyl ethyl ether	18.5	190.0	136.15	0.9509	143.18
Methyl eugenol	18.7	249.0	178.22	1.0386	171.59
Piperitone	18.7	234.0	152.23	0.9324	163.26
Jasmone	18.8	258.0	164.24	0.9437	174.03
Methyl chavicol	18.8	215.0	148.20	0.9720	152.46
Dibenzyl ether	19.0	297.0	198.25	1.0341	191.71
Carvone	19.1	231.0	150.21	0.9645	155.73
Isoamyl benzoate	19.1	262.0	192.25	0.9930	193.60
Methyl heptine carbonate	19.2	216.8	154.21	0.9232	167.03
Triacetin	19.3	259.0	218.20	1.1562	188.72
Anethole	19.5	234.0	148.20	0.9860	150.30
Methyl isoeugenol	19.5	270.0	178.22	1.0568	168.64
Safrole	19.6	233.0	162.18	1.0960	147.97
Diphenyl oxide	19.7	259.0	170.20	1.0750	158.32
Benzyl propionate	19.8	222.0	164.17	1.0360	158.46
Eugenol acetate	19.8	282.0	206.23	1.0842	190.21
Phenylethyl acetate	20.1	232.0	164.16	1.0380	158.15
Cinnamyl acetate	20.2	262.0	176.17	1.0186	172.95
Propriophenone	20.2	218.0	134.17	1.0105	132.77
p-Cresyl acetate	20.4	209.0	150.17	1.0512	142.85
p-Methyl acetophenone	20.4	226.7	134.17	1.0061	133.48
Benzyl acetate	20.5	213.0	150.17	1.0500	143.01
Ethyl acetoacetate	20.5	180.8	130.14	1.0213	127.42
Ethyl benzoate	20.5	212.0	150.17	1.0500	143.01
Isosafrole	20.5	253.0	162.18	1.1206	144.72
Ethyl cinnamate	20.7	271.0	176.18	1.0490	167.95
Acetophenone	21.0	202.0	120.15	1.0330	116.31
Benzyl benzoate	21.0	324.0	212.24	1.1180	189.83
p-Methoxyacetophenone	21.1	258.0	150.17	1.0818	138.81
Methyl cinnamate	21.2	263.0	162.18	1.0415	155.71
Benzyl formate	21.4	203.0	136.19	1.0810	125.98
Methyl benzoate	21.4	200.0	136.14	1.0940	124.44

Figure 2. Ethylene brassylate
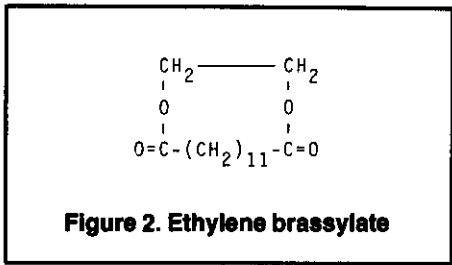
An Experiment

Leaving the realm of the theoretical for a moment, we can apply what we know to attempt an application. One of the ways PVC can be processed is as a plastisol. A plastisol is a suspension of a fine PVC powder called a "dispersion resin" in plasticizer. These plastisols are viscous liquids that can be stable for over a month. The large molecular weight of the plasticizer drastically slows diffusion into the PVC, even though they are good solvents. However, when a plastisol is heated it first gels and then fuses into a tough, flexible polymer. Plastisols are widely used to make upholstery, toys, flooring, wire dish drainers, and many other items. To prove a point, we can formulate a plastisol with no ordinary plasticizer at all and use a fragrance chemical instead. See formula 1.

The term "phr" means "parts of whatever per hundred parts of resin by weight." The last three items are synergistic thermal stabilizers. A total of 25 grams was prepared, vacuum degassed, and poured into two aluminum foil dishes that had been sprayed with mold release. The samples were then baked at 177°C for twenty minutes. This produced two disks of tough, flexible polymer that smelled like musk and, with the exception of a few air bubbles, were clear and homogeneous.

Before leaving this topic it should be noted that a real plastisol could also contain pigments, flame retardants, air release agents, viscosity stabilizers, blending resins, fungicides, UV stabilizers, and anti-blocking agents. Also, it may be possible

Table II. Group Values Used in Calculating the Solubility Parameter[6]

Group	Bond Type	Value
$-CH_3$	Saturated	303.3
$-CH_2-$	Saturated	269.0
$>CH-$	Saturated	175.9
$>C<$	Saturated	65.5
$CH_2=$	Alkene	258.8
$-CH=$	Alkene	248.5
$>C=$	Alkene	172.8
$-CH=$	Aromatic	239.9
$>C=$	Aromatic	200.7
$-O-$	Ether	235.2
$-O-$	Acetal	236.3
$-O-$	Epoxide	360.4
$-COO-$	Ester	668.1
$>C=O$	Ketone	538.0
$-CHO$	Aldehyde	598.6
$>(CO)_2O$	Anhydride	1160.4
$-COOH$	Acid	564.8
$-OH \rightarrow$	H-Bond OH	485.8
$-OH$	Primary (Not H-Bonded)	637.8
$-OH$	Secondary	591.6
$-OH$	Tertiary	798.6
$-OH$	Phenolic	349.8
NH_2	Amino 1 degree	463.5
$-NH-$	Amino 2 degrees	368.2
$>N-$	Amino 3 degrees	125.0
$-C\equiv N$	Nitrile	725.3
$-NCO$	Isocyananate	733.7
$HCON<$	Formamide	1017.0
$-CONH-$	Amide	1134.6
$-CONH_2$	Amide	1206.6
$OCONH$	Urethane	1261.9
$-S-$	Thioether	428.3
Cl	Primary	419.5
Cl	Secondary	426.1
Cl_2	Twinned	701.0
Cl	Aromatic	329.3
Br	Primary	527.5
Br	Aromatic	420.6
F	Primary	84.5
Structural features:		
Conjugation		47.6
Cis		-14.6
Trans		-27.6
4 Member Ring		159.1
5 Member Ring		42.9
6 Member Ring		-47.9
7 Member Ring		92.3
Bicycloheptane Ring		46.1
Tricyclodecane Ring		127.8
Ortho Substitutions		19.8
Meta Substitutions		13.5
Para Substitutions		82.4

Formula 1

Geon 121 vinyl dispersion resin (a)	100
Emeressence 1150 ethyle brassylate (b)	100 phr
Plas-Chek 775 epoxidized soybean oil (c)	5 phr
Therm-Chek 760X calcium/zinc stearate paste (c)	3 phr
Therm-Chek 5526 phosphite chelator (c)	1 phr

a. B.F. Goodrich Chemical Group
b. Emery Industries, Inc.
c. Ferro Corporation, Bedford Chemical Division

to incorporate small amounts of aldehydes, even though they are strong hydrogen bonders, but they show poor oxidation stability. An aldehyde that works in a plastisol may fail in PVC with a longer heat history such as that used for extrusion or injection molding.

Perfume Blends

The solubility parameter for a mixture, δ mix, is just the sum of the volume fraction of each component (X_i) times the solubility parameter of each component, δ_i:

$$\delta_{mix} = X_1\delta_1 + X_2\delta_2 + \ldots X_i\delta_i$$

For instance, if a large quantity of phenyl methyl carbinyl acetate (styrallyl acetate) is desired in a formula for PVC, its low solubility parameter can be compensated for by pairing it with benzyl acetate or an ordinary plasticizer with high solubility parameter.

Conclusion

It has been shown that by considering the implications of solubility theory, polymers con-
taining 50% fragrance can be made. And although the concentration has been on PVC, both because of its importance and for the tutorial value of having a concrete example, the principles discussed can be applied to any polymer.

References

Address correspondence to Martin G. Meder, 121 Park Avenue, Hightstown, NJ 08520, U.S.A.

1. J. A. Brydson, Plastics Materials, 4th Ed., Butterworth Scientific, Boston, 1982
2. A. F. M. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, 1983
3. J. Branderup & E. H. Immergut, eds., Polymer Handbook, 2nd Ed., John Wiley & Sons, New York, 1975, IV-337
4. Ibid.
5. F. M. Fowkes, et al., Acid-Base Complexes of Polymers, J. Poly. Sci., Poly Chem. Ed., **22**, 547-566, 1984
6. K. L. Hoy, Tables of Solubility Parameters, Union Carbide Corporation, Solvents and Coatings Materials Division, Bound Brook, NJ, 1975