

A Primer on Perfuming Polymers—Part II

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The first article in this series addressed the question of how to find fragrance chemicals that can be successfully incorporated into a specific polymer (polyvinylchloride).¹ This paper will consider the opposite situation—given a specific fragrance, how can a polymer be selected to contain it?

The fragrance that will be considered is vanilla because of the warm feeling it can give to many products. Also, the vanilla fragrance is produced by chemicals with strong hydrogen bonding ability and a Lewis acid character, which will provide contrast against the results obtained from perfume chemicals with moderate hydrogen bonding ability and Lewis base character discussed the last time. Also, vanilla has a low vapor pressure which demands heroic measures to get enough vanilla into a composition to get any appreciable “lift-off.”

As a further departure from the prior paper, the type of polymer host considered is one that can be fabricated into a label adhesive. Labels generally have large surface areas available for radiating fragrance, and they are the only opportunity to influence a customer that doesn't open bottles in the store.

Background on Vanilla

Three materials are commonly used to produce the primary vanilla effect.

- **Vanillin.** 4-Hydroxy-3-methoxybenzaldehyde, $T_m = 82^\circ\text{C}$, $T_b = 285^\circ\text{C}$, MW = 152.16 g/mole. Vanillin is the standard of comparison against which the other materials compete with respect to price, odor quality and stability. The

phenolic hydrogen has a positive, Lewis acid quality which hydrogen bonds to the unshared pair of electrons (negative, Lewis base) on the aldehydic oxygen of adjacent vanillin molecules. This intermolecular bonding helps explain why an organic compound with a relatively low molecular weight can have such a high melting point. Hydrogen bonding may also occur to a lesser extent with the ether oxygen of the methoxy group.

- **Ethyl Vanillin.** 4-Hydroxy-3-ethoxybenzaldehyde, $T_m = 77^\circ\text{C}$, MW = 166.18 g/mole. Ethyl vanillin has a sweeter smell than vanillin and is generally considered to have four times the odor strength of vanillin. The price is only double that of vanillin, which explains the commercial popularity of this material.
- **Ethyl Vanillin Propylene Glycol Acetal,** MW = 178.24. Ethyl vanillin PG acetal has a lower odor intensity than the parent compound, but this is offset by the gain in stability yielded by the protection of the aldehyde group.

For ease of dissolution in a solvent (ordinary or polymeric), it is always desirable that the solute be a liquid because the heat of crystallization of a solid solute does not have to be overcome before dissolution can occur. The liquid solute would also eliminate the tendency (in a thermodynamic sense) for reprecipitation of the solute. In other words, it would be helpful if vanillin and ethyl vanillin could be liquid or close to being liquid in order to dissolve the largest possible amount of these materials in a polymer/solvent matrix.

The liquids required can be formed by a eutectic composition of vanillin and ethyl vanillin.

A eutectic composition denotes a two-phase material which melts congruently (all at once) at a temperature less than the melting point of either component alone. It can be thought of as the mix ratio where the vanillin dissolved in the ethyl vanillin interferes with the crystal structure of the ethyl vanillin as much as the ethyl vanillin dissolved in the vanillin ruins the vanillin's crystal structure.

For compounds of very similar structure like vanillin and ethyl vanillin, this not surprisingly occurs in an equimolar mixture. The melting point of vanillin is 86.6°C at maximum endotherm (measured with a Perkin-Elmer DSC-2B differential scanning calorimeter) and has a heat of melting of 40.0 cal/g. The corresponding values for ethyl vanillin are 82.4°C and 40.3 cal/g respectively. The melting point for "vanilla eutectic" is 50.8°C and the heat of melting is 1.5 cal/g. While not quite a liquid, it will be seen that vanilla eutectic has advantages.

Background on Polymers

Polymers used for label adhesives on consumer products fall into two related categories:

solvent based and hot melt. Variations for delayed use include:

- put a solvent based adhesive on a label, let dry, then heat seal later
- put an aqueous solvent based adhesive on a label, let dry, then moisture activate later
- put on something that never quite hardens (i.e., a pressure sensitive adhesive), then use anytime.

While the latter method is the one that is most convenient, the labels don't generally stick as well as those using the former methods in conjunction with a commercial labeling machine.

One desirable characteristic that has become important lately, even for hot melt adhesives, is water solubility. This allows for easy recycling of plastic bottles and easy repulping of magazines (bindings) and paperback books.

Water soluble polymers have the highest hydrogen bonding ability of any polymers and may be ideal candidates for perfume materials with high hydrogen bonding ability. This is indicated for vanillin by its slight water solubility. The polymers used are polyvinylalcohol, polyvinylpyrrolidone and polyethyloxazoline. These polymers may be thought of as chains of many identical connected links called "mers."

- *Polyvinylalcohol* (PVOH). MW of a mer = 44.05. The only good solvent for this plastic is water, although up to 35% ethanol can be added after dissolution without causing precipitation. Unplasticized PVOH decomposes at 150°C before melting. Even plasticized PVOH can only be compression molded because of its very high melt viscosity. (Dupont Elvanol 90-50 was used in this evaluation.)
- *Polyvinylpyrrolidone* (PVP). MW of a mer = 111.14. Many polar solvents will dissolve PVP. This polymer will decompose at 175°C prior to melting. (GAF PVPK 30 was used.)
- *Polyethyloxazoline* (PEOX). MW of a mer = 99.13. This plastic may be considered a polymeric analog of N,N-Dimethylacetamide and dissolves in a wide range of solvents. It softens at 70°C and does not decompose until 380°C, so it can be used in hot melt as well as solvent-based systems. (Dow Chemical XAS 10874.01 was used.)

Experimental

The 1g of each polymer was dissolved in 2g water except PVOH which was dissolved in 5g water. Vanilla eutectic was added at 0.9 mole fraction with respect to mer molecular weight as a 50wt% stock solution in ethanol. Ethyl vanillin

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PG acetal was added neat at 90 mole%. PVOH received only 50 mole% vanilla eutectic as it was felt that hemiacetal formation would limit solubility. Ethyl vanillin PG acetal was not tried with PVOH. The mixtures were poured into petri dishes and placed in an 85°C oven for 4 hours, removed and allowed to cool.

Initial Results

Both compositions containing ethyl vanillin PG acetal were too liquid to be useful. PVOH excluded vanilla eutectic. PVP-vanilla eutectic showed good tack and lift-off, but it had a definite yellow color. PEOX-vanilla eutectic had good tack, clarity and lift-off. Neither the PVP or the PEOX-vanilla eutectic compositions were water soluble. Because the PEOX composition had the potential of being used as a hot melt and it was water white in thin films, it was selected for further study. Specifically, a water soluble composition should be possible at a lower concentration of vanillin because the pure polymer is water soluble. A 40wt% solution of PEOX in water should have solvent properties similar to a solution of N,N-Dimethylacetamide in water (see structure of PEOX, figure 1). This solution has the same solubility parameter as a 38wt% ethanol solution in water, and that should be able to dissolve at least 10g vanillin per 100g solution.

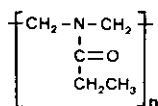


Figure 1. Polyethyloxazoline (PEOX)

More Experimental

Six samples were prepared by adding molten vanilla eutectic at 65°C, 0.1 to 0.6g, to 2.5g of 40wt% PEOX aqueous solution with stirring at room temperature. Bottles containing up to 0.3g vanilla eutectic cleared rapidly, and while 0.4g (corresponding to 16g vanilla eutectic per 100g solution) did eventually dissolve, it was more difficult. Higher quantities were obviously insoluble. When 0.3g ethyl vanillin was added to 2.5g of solution, it was apparent that very little dissolved and that is the reason that it was necessary to develop the vanilla eutectic. Since a degree of water tolerance is always desirable in a commercial adhesive, the mix corresponding to 0.3g vanilla eutectic is preferable to one with the maximum amount of dissolved material.

Discussion

The final result is shown in Formula 1. Note that the solution is 46% solids and the vanilla eutectic is 23% of the dry weight. Possible variations on the formula include elimination of the water for use as a hot melt adhesive. This would require the use of a nitrogen blanket above the adhesive in a labeling machine to prevent oxidation of aldehyde groups in the vanilla eutectic.

Formula 1. Vanillin Fragranced Label Adhesive

	<u>Grams</u>
Vanillin	51
Ethyl Vanillin	56
Polyethyloxazoline	
(Dow Chemical XAS 10874.01)	357
Water	536

Another change could be substitution of ethanol for water to provide quicker drying times. Addition of certain surfactants would improve adhesion to difficult to-wet surfaces like polyolefins.

The PEOX used has a molecular weight of 50,000, but grades are available up to 500,000 MW. Use of this grade would increase green tack, but at a price of introducing stringiness to the formula. Aqueous solutions of PEOX show good adhesion to aluminum, cellophane, nylon, acrylic, polyester, glass, and paper.³

In summation, it can be seen that polymer hosts can be found for even highly polar, crystalline fragrance materials. A narrow category (label adhesives) was selected for maximum specificity for tutorial value. However, the same kind of thinking, for example, could have been used to find a structural polymer to make a sugar bowl that continuously makes vanilla sugar from sugar.

References

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