

## Using Solubility Parameters for Material Selection

### Introduction

We want to assess what sort of thermoplastic polymer we can use for containment of toluene at ambient conditions. A special design requirement is prevention of plasticizing of the material by toluene. This requirement is related to diffusion resistance: in many instances plasticizing causes the initial diffusion rate to increase several orders of magnitudes. This can be noticed from the figures in the table for liquid diffusion on the website. If a chemical has a high solubility in the polymer then the weighted average diffusion rate ( $D$ ) becomes much larger than the initial rate ( $D_0$ ).

Taking the above considerations into account, we decided to use the solubility parameter concept. We obtained the solubility parameter figures of toluene and eight polymers, distinguishing in a dispersion, dipole-dipole and hydrogen-bonding component. Then, we positioned toluene and the engineering polymers in a triangular graph. The graph is depicted below. The positions in the graph are according to the relative value of the three solubility components. Realize that the three axis values of each position in the graph add up to a total of 100%.

### Theory

For decades Hildebrand solubility parameters have been used to predict the solubility of solvents in polymers. If the exact solubility of a solvent is unknown, the Hildebrand parameters are useful to acquire an indication of the solubility and swelling behaviour of the polymer under the load of a specific solvent.

The total Hildebrand parameter (symbol:  $\delta$ ) is a result of the following intermolecular forces, so called Van der Waals forces: dispersion ( $\delta_d$ ), dipole - dipole ( $\delta_p$ ) and hydrogen bonding ( $\delta_h$ ). The total Hildebrand parameter can be calculated from these components as follows:

$$\delta = [ \delta_d^2 + \delta_p^2 + \delta_h^2 ]^{0.5}$$

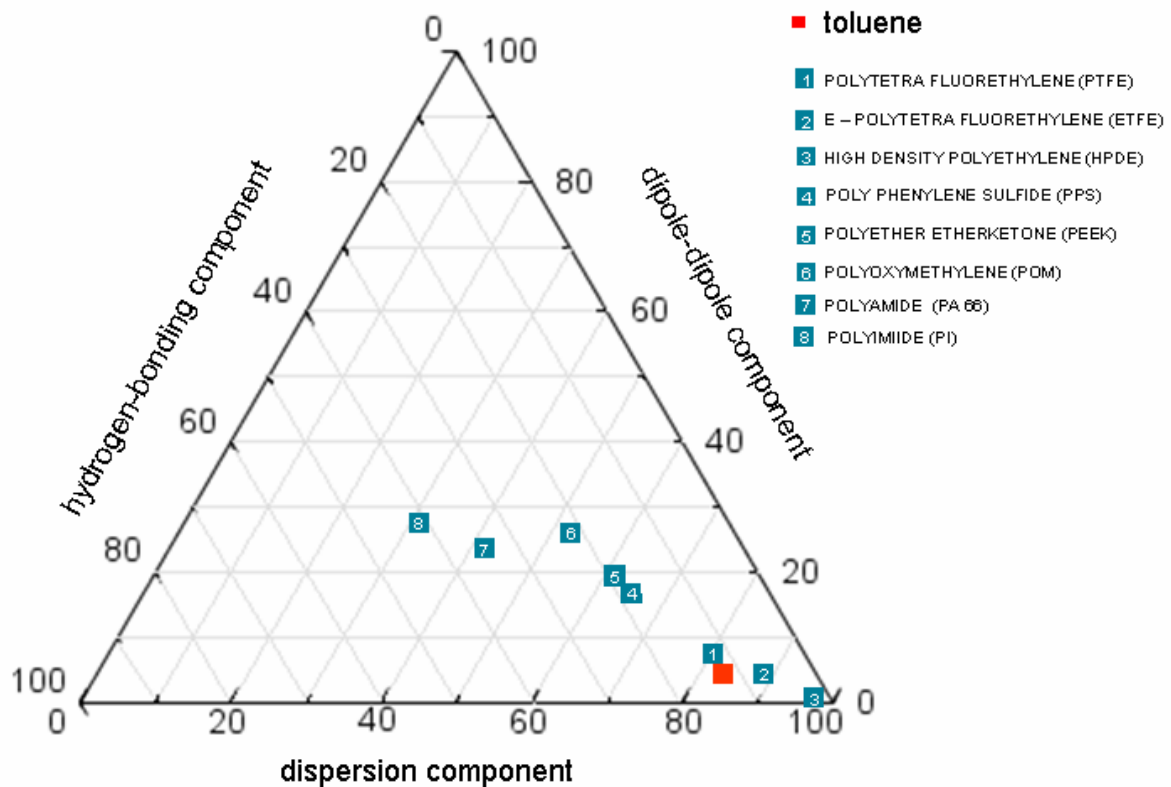
When a solvent and a polymer have a solubility parameter that (closely) resembles, the solubility of the solvent in the polymer is high. The explanation is as follows. Fundamental thermodynamics states that mixing of species usually consumes heat (appears with a positive sign in our equations) and produces entropy (entropy is a measure for chaos, negative sign). Here we can assume that heat of mixing and entropy multiplied by temperature, are balanced in case of system equilibrium. This equilibrium determines the relative concentrations of the substances involved. The change in heat of mixing can be calculated using the species solubility parameters. In formula this is expressed as follows:

$$\Delta H_{\text{mixing}} = + [\delta_{\text{polymer}} - \delta_{\text{solvent}}]^2 \times [\text{vol\% polymer} \times \text{vol\% solvent}] \times [\text{total volume}]$$

Notice from this expression that consumption of heat is small when the difference between parameters is small. Furthermore, realize that heat of mixing increases with the square of the parameter difference, and as such, solubility is also a non linear function of this difference. When heat of mixing is high, only high temperatures will drive the

entropy to a sufficient level that can compete with the heat of mixing. It is therefore that solubility usually increases with temperature.

## Graphical Analysis



If toluene is positioned on a short distance from polymers, the specie has a high solubility. Examples are PTFE, ETFE and HDPE. Positioning on a large distance, results in low solubility. Hence, we decided to advice several kinds of polyimide for toluene containment.