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[P9]-A generic solvent selection methodology for the model-based design of a coating formulation

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It is known that solvents account for one third of the cost in coating formulations and are extremely important in order to deliver the active ingredient (pigment and binder) of the formulation. They are vital in conferring the final aesthetic and functional properties of the coating [1]. Therefore, the selection of the solvent mixture is a critical step in coating formulation design.
A generic solvent selection methodology for the model-based design of coating formulations is developed in order to aid a formulation chemist to quickly arrive at a solvent mixture with the desired physico-chemical and environmental, health and safety (EH&S) properties. Such a model-based methodology is useful as it can reduce the search space for the solvent mixture. The applicability of this algorithm has been tested via a case-study on solvent mixture design for an acrylic-based organic coating.

Introduction

Selection of the right ingredients including solvents and calculation of their amounts and composition in the final formulation, is a critical step in coating product design. To perform this task efficiently, if the potential of model-based computer-aided tools that can perform a fast screening of numerous candidates can be used, then the amount of resources required for experimentation can be spared. However, the computer-aided procedures cannot suffice by themselves. They are required to be supplemented with verification using experimental procedures. Hence, the computer-aided stage is used only to speed-up the formulation design process and serve as a guidance for a formulation chemist.

A Generic Model-based Methodology for Solvent Selection

A generic model-based methodology for solvent selection has been developed. The steps in the methodology are shown in Figure 1. In this methodology, first the problem is formulated wherein the constraints on solvent-related physico-chemical properties are set. A binary solvent mixture is then designed using a database of solvents containing pure component properties, group-contribution property models and mixing rules. The UNIFAC activity coefficient model is used to determine the miscibility of two solvents.
Next, the compatibility of the designed solvent mixture with the polymers is checked using the 'Hansen Solubility Sphere' calculations. The Hansen Solubility Parameters of the polymer ($\delta_{d,pol}$, $\delta_{p,pol}$, $\delta_{h,pol}$) can be retrieved from polymer database and used to calculate the ratio of solvent – polymer distance in Hansen space, $R_{a,pol}$ to polymer radius of interaction, $R_{o,pol}$. This ratio is denoted by RED_{pol} and is given by Eq. 1. A RED_{pol} value less than 1, indicates a good polymer-solvent solubility.

$$RED_{pol} = \frac{R_{a,pol}}{R_{o,pol}} = \frac{\sqrt{4\left(\delta_{d,pol}-\delta_{d,sol}\right)^2+\left(\delta_{p,pol}-\delta_{p,sol}\right)^2+\left(\delta_{h,pol}-\delta_{h,sol}\right)^2}}{R_{o,pol}} \quad (1)$$

Similarly, the RED_{pig} is given by Eq. 2. The RED_{pig} value is required to be greater than 1 denoting that the solvent mixture is a poor solvent for the pigment particles and hence will facilatate the dispersion of the pigment particles.

$$RED_{pig} = \frac{R_{a,pig}}{R_{o,pig}} = \frac{\sqrt{4\left(\delta_{d,pig}-\delta_{d,sol}\right)^2+\left(\delta_{p,pig}-\delta_{p,sol}\right)^2+\left(\delta_{h,pig}-\delta_{h,sol}\right)^2}}{R_{o,pig}} \quad (2)$$

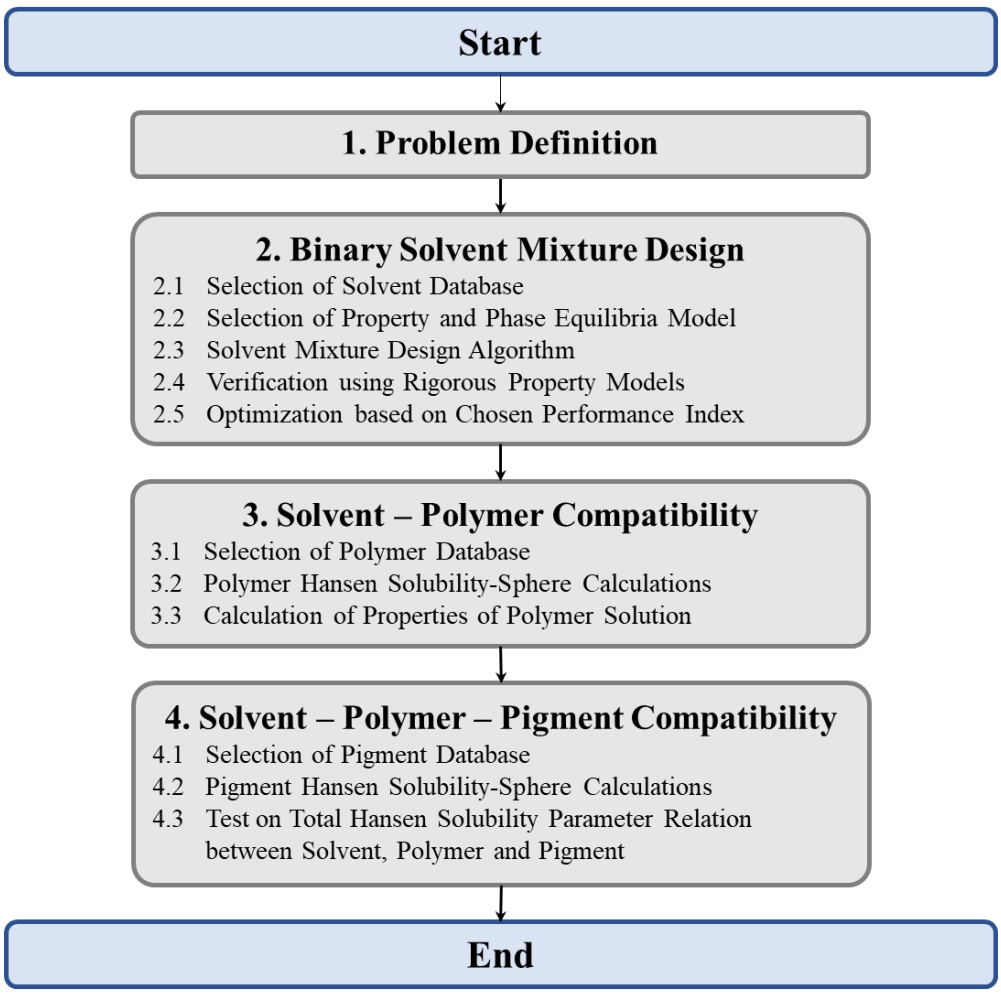

Figure 1: Model-based Solvent Selection Methodology

Additionally, the total HSP of the pigment must lie in between the total HSP of the polymer and the solvent mixture, in order to yield a stable coating formulation [2]. Therefore, if all the conditions to test the compatibility of the designed solvent mixture (from Step 2) with the polymer and the pigment are satisfied, the solvent selection is deemed appropriate and the end of the methodology is reached.

Results and Discussions

It is desired to design a water-insoluble binary solvent mixture for an acrylic paint containing an organic pigment. Three property databases have been compiled using handbooks and peer-reviewed articles [2-4]. The solvent database consists of 31 water insoluble solvents which can yield 465 binary solvent mixtures. The acrylic polymer database contains the properties of two polymers namely polymethyl methacrylate (PMMA) and polyethyl methacrylate (PEMA). The pigment database contains the HSP and the radius of solubility, $R_{o,pig}$ for six organic pigments.

The first step of the methodology is to formulate the problem. This is done as shown in Table 1.
Considering the constraints shown in the 'Solvent' section of Table 1, binary solvent mixtures are designed using the ProCAPD tool [5]. 41 binary solvent mixtures satisfied the constraints on viscosity, molar volume surface tension and the Gibbs energy of mixing. Additionally, only four out of the 41 designed binary solvent mixtures also satisfied the constraints on the HSP.

Thereafter, the RED_{pol} was evaluated using Eq.1. When using PMMA as the polymer only one solvent mixture namely, 'Acetic acid, butyl ester + butyrolactone' yielded a RED_{pol} value of less than 1. While, when using PEMA as the polymer, the following four solvent mixtures gave a RED_{pol} value of less than 1.

Table 1: Problem Formulation

	Need	Target Properties	Constraints
Solvent			
1.	Solubilize polymer	Hansen Solubility Parameters of solvent, $\delta_{d,pol}$, $\delta_{p,pol}$, $\delta_{h,pol}$	$\delta_{p,pol} - 3 < \delta_{p,sol}$ (MPa^{½}) $< \delta_{p,pol} + 3$ $\delta_{d,pol} - 3 < \delta_{d,sol}$ (MPa^{½}) $< \delta_{d,pol} + 3$ $\delta_{h,pol} - 3 < \delta_{h,sol}$ (MPa^{½}) $< \delta_{h,pol} + 3$
2.	Easily flowable	Viscosity, η	$0.6 < \eta$ (cP) < 0.9
3.	Good spreadability on surfaces	Molar Volume, V_m Surface Tension, σ	$100 < V_m$ (l.kmol^{-1}) < 130 $26.5 < \sigma$ (mN.m^{-1}) < 29.5
4.	Good Stability	Gibbs Energy of Mixing	$\Delta G_{mix}/RT < 0$
Solvent-Polymer Mixture			
1.	Solvent – Polymer Solubility	Solubility Parameter Distance, $R_{a,pol}$ Radius of Solubility, $R_{o,pol}$	$R_{a,pol} = \sqrt{4(\delta_{d,pol} - \delta_{d.sol})^2 + (\delta_{p,pol} - \delta_{p,sol})^2 + (\delta_{h,pol} - \delta_{h,sol})^2} \leq R_{o,pol}$

The four identified solvent mixtures are,

i) Acetic acid, ethyl ester (1) + cyclohexanone (2), $x_1 = 0.72$

ii) Acetic acid, hexyl ester (1) + dichloromethane (2), $x_1 = 0.52$

iii) Dichloromethane (1) + Ethanol, 2-butoxy-, acetate (2), $x_1 = 0.67$

iv) Acetic acid, butyl ester (1) + butyrolactone (2), $x_1 = 0.78$

Further, the RED_{pig} value using Eq.2. is also calculated. Considering that the total HSP of the pigment must lie between the total HSP of the polymer and the solvent mixture, the suitable solvent - polymer mixtures for three out of the six organic pigments in the database are found. The results are summarized in Table 2.

Table 2: Suitable Binary Solvent Mixtures and Polymer for three Organic Pigments

Sr. No.	Organic Pigment	Binary Solvent Mixture and Polymer
1.	Palitol Gelb L1820 BASF	Solvent Mixture iv) and PMMA polymer
2.	Heliogen Blau 6930L BASF	Solvent Mixture i) or iii) and PEMA polymer
3.	Perm Lackrot LC Hoechst	Solvent Mixture iv) and PMMA polymer

Conclusion and Future Work

Therefore, a generic model-based methodology for the design and selection of solvents for coating formulations has been developed. The methodology has been applied to select the solvent for an acrylic coating. However, the methodology needs to be improved in order to account for the interactions in a practical formulation. Besides, rigorous thermodynamic property models must be used to verify the final properties. Also, the EH&S properties should be checked, in order to arrive at safe and sustainable coating solutions.

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