

# Distribution of organic additives such as plasticisers during dissolution-precipitation polymer recycling

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## 1. Introduction

One of the many possible pathways for polymer recycling is dissolution-precipitation. In this process, the polymer is ground, dissolved in a suitable solvent, cleaned, typically via filtration, precipitated by solvent evaporation or nonsolvent addition, dried and finally extruded (Pappa *et al.*, 2001). The solvent and nonsolvent are then separated through distillation and reused. A typical full process flowheet is schematically represented in Figure 1.

The output of this process is a pure polymer is from which the mechanical, thermal and molecular properties are not significantly affected (Achilias *et al.*, 2009; Pappa *et al.*, 2001). This procedure has proven to be capable of selective dissolution of polymers from multilayer packaging, as well as other composite materials (Kaiser *et al.*, 2018). Generally, a 3/1 volumetric ratio of nonsolvent to solvent is used in this process to achieve sufficient polymer precipitation, which necessitates an energy intensive solvent-nonsolvent separation (Ügdüler *et al.*, 2020). Since the drying of the precipitate polymer is also energy intensive, it is important to know how solvent and nonsolvent are distributing throughout the process steps and consequently how they can be recovered and removed from the polymer matrix. Ternary diagrams for polymers, solvent and nonsolvent systems, which are mostly used for membrane production, provide this insight and can be used to optimise the process. It is possible to produce said diagrams using the extended Flory-Huggins solutions theory (Romay *et al.*, 2021).

Besides the energy consumption, there have been issues with the removal of certain additives. An example is the VinyLoop plant in Italy, which recycled flexible polyvinylchloride (PVC) cables through dissolution precipitation. The plant was closed in 2018 due to its inability to remove diethylhexyl phthalate (DEHP) from the recycle (CreaCycle, n.d.; Plastech, 2018). DEHP, amongst other phthalate plasticisers, has been restricted in PVC under the EU's REACH legislation (PlastEurope, 2018). Therefore, the presented research analyses the phase distribution of solvents and additives throughout the dissolution-precipitation process, at different process conditions.

## 2. Theoretical background

According to the extended Flory-Huggins solutions theory, the Gibbs free energy of mixing,  $\Delta G_m$ , for ternary systems can be calculated using the following equation (Barzin and Sadatnia, 2007):

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_2)n_1\phi_2 + \chi_{13}n_1\phi_3 + \chi_{23}n_2\phi_3 \quad (1)$$

In this equation  $R$  is the gas constant,  $T$  the absolute temperature and  $n_i$  and  $\phi_i$  are the number of moles and volume fraction of component  $i$  respectively, where  $i$  refers to nonsolvent (1), solvent (2) or polymer (3).  $g_{12}$  represents the binary interaction parameter between the solvent and nonsolvent. It is widely accepted that only  $g_{12}$  is concentration dependent, expressed as a function of  $u_2 = \phi_2/(\phi_1 + \phi_2)$ , while  $\chi_{13}$  and  $\chi_{23}$  can be considered as constants. It is possible to calculate  $g_{12}$  based on activity coefficients obtained through COSMO-RS and both  $\chi_{13}$  and  $\chi_{23}$  can be calculated with Hansen Solubility Parameters.

When liquid-liquid demixing occurs, a polymer rich and a polymer poor phase are formed and the three components in the ternary system are distributed between these two phases. These phases are in thermodynamic equilibrium and thus both lie on the binodal curve. The chemical potential is used to define this equilibrium:  $\Delta\mu_{i,a} = \Delta\mu_{i,b}$ , where  $a$  denotes the polymer rich phase and  $b$  the polymer poor phase. The chemical potential for each component can be calculated using equation 2, which is the partial derivative of equation 1.

$$\frac{\Delta\mu_i}{RT} = \frac{\partial}{\partial n_i} \left( \frac{\Delta G_m}{RT} \right)_{P,T,n_j} \quad (2)$$

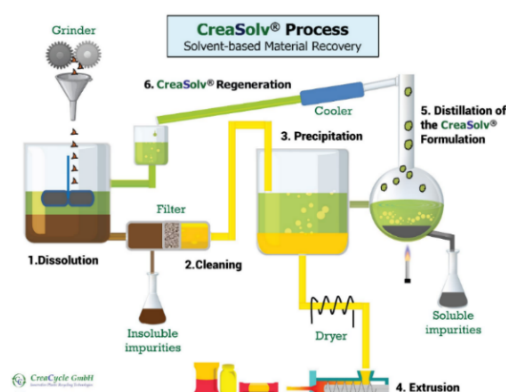


Figure 1: Dissolution-precipitation process (CreaCycle, 2018)

Adding the mass balance for each phase, results in five equations and six unknown concentrations. By selecting the polymer concentration of the polymer lean phase ( $\phi_{3,b}$ ) as an independent variable, the remaining concentrations can be calculated. This was done using the Newton-Raphson method in MATLAB.

### 3. Materials and methods

PVC purchased from Sigma-Aldrich, with an  $M_w$  of 80,000 and  $M_n$  of 47,000 g/mol, was used. The plasticisers DEHP and di(2-ethylhexyl) terephthalate (DEHT) were purchased from Chem-Lab (>99%) and Acros Organics (>97%) respectively. The solvents cyclohexanone, THF and 2-methyltetrahydrofuran were purchased from Chem-Lab with a purity >99%, >99.9% and >99% respectively. Ethanol and n-hexane were applied as nonsolvents and were obtained through Chem-Lab with purities >99% and water was double-distilled.

The characterization of the plasticizers was performed with an Agilent GC-MS 6890 with an Agilent J&W HP-5MS 30m x 0.250mm (0.25 $\mu$ m film thickness) column. The following temperature profile was applied: 50 °C for 1 minute, 30 °C/min to 280 °C, 15 °C/min to 310 °C and 5 minutes hold (Bushey, 2018).

### 4. Results and discussion

Figure 2 represents a ternary diagram produced with the Flory-Huggins solutions theory for a system with PVC, cyclohexanone and ethanol. The black line represent the binodal (eq. 2) and the red lines represent different tie-lines. These tie-lines predict the composition of the polymer rich and poor phases. Based on this theory accompanied by experiments, it is possible to get an estimate about the solvent encapsulation within the polymer precipitate, which is important for post-drying steps and also influences the partitioning of additives.

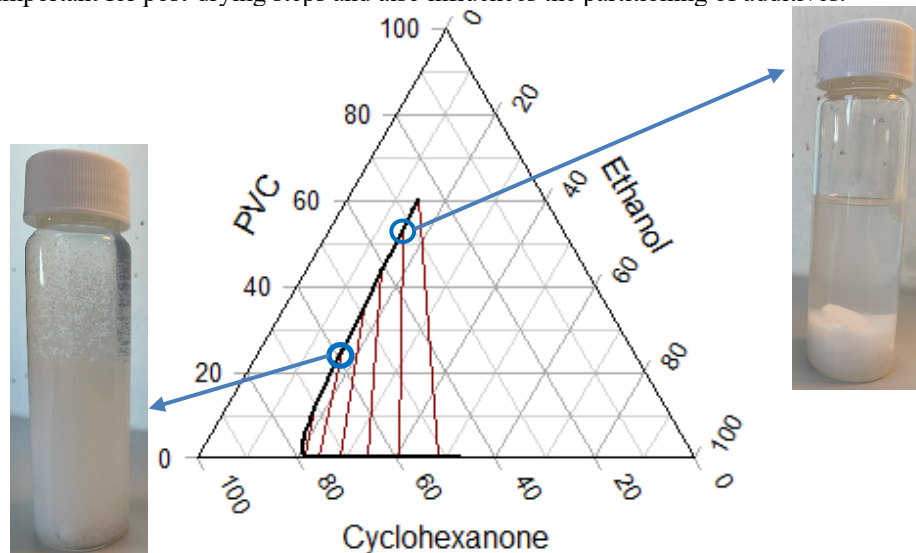


Figure 2: Ternary diagram for PVC-Cyclohexanone-EtOH; black line = binodal curve; red lines = tie-lines

Due to the presence of legacy additives (e.g. lead-based additives and phthalates), which are now restricted or even forbidden, it is important to achieve high polymer purities. Therefore it is crucial to know the effect of different process parameters on the distribution of additives between the (solid) polymer rich phase and (liquid) polymer poor phase. This presentation focuses on the quality of the recycled polymer after dissolution recycling, based on the theoretical background of polymer precipitation. Next to this, the partitioning of additives and thus final concentrations of additives in the final recycled polymer will be presented for different solvent-nonsolvent combinations.

### 5. Acknowledgement

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