

Modelling the dissolution kinetics of plasticised poly(vinyl chloride)

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Keywords: Modelling, Polymer dissolution, Plastic recycling

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1. Introduction

The dissolution of polymers is a complex problem which has been investigated for decades, but is not yet fully understood (Miller-Chou and Koenig, 2003; Valois et al., 2016). In the production of polymers, dissolution has always been a key step, be it for extrusion or for blending with additives. More recently, however, polymer dissolution has been a topic which has come back on the agenda in a different context, mainly as a means of recycling solid plastic waste (Ügdüler et al., 2020; Zhao et al., 2018). Solvent-based recycling allows for the chemical structure of the polymer to be preserved, whilst also removing additives (e.g. fire-retardants, plasticisers, etc.). This recycling process could thus result in a recycled polymer of near-virgin grade without breaking the original product apart. A successful recycling of bulk polymers like poly(vinyl chloride) (PVC), has the potential capability to drastically cut the energy consumption and resource need in the plastics industry.

The construction of a kinetic model based on the phenomenology of polymer dissolution has also been widely discussed in literature (Miller-Chou and Koenig, 2003). Narasimhan and Peppas concluded that although all models address some aspects of polymer dissolution, no model has been able to completely predict the dissolution behaviour without fitting model parameters to experimental input (Narasimhan and Peppas, 1997). This work tries to take known concepts in literature and incorporate them into kinetic models for the dissolution of plasticised PVC with the aim to have a balance between model accuracy and ease of use.

2. Kinetic models

Two kinetic dissolution models are proposed in this work. The first model is derived based on a mass balance of a polymeric particle. It is assumed that the disentanglement rate k_d [m/s] is the rate determining step, which is based on findings for stirred solutions reported by Ranade and Mashelkar (Ranade and Mashelkar, 1995). An expression for the disentanglement rate can be formulated based on findings from different authors (Ranade and Mashelkar, 1995; Valois et al., 2016). The radius of the polymeric particle can be found by incorporating the disentanglement rate into the mass balance and integrating the resulting differential equation. The weight fraction of polymer dissolved ω_2 is given by Eq 1.

$$\omega_2 = \omega_{2,0} \left(1 - \frac{4k_0 T \exp(-E_a/RT)}{3\eta_1 r_0^{4/3}} t \right)^{\frac{9}{4}} \quad (1)$$

Where, k_0 [(Pa.m¹⁻ⁿ)/K] is a pre-exponential factor, T [K] is the temperature, n [-] is an exponent, E_a [J/mol] is the activation energy, R [J/(K.mol)] is the universal gas constant, t [s] is the time taken, η_1 is the solvent viscosity, $\omega_{2,0}$ is the steady state weight fraction value and r_0 is the initial particle size.

The second model, given in Eq 2, is more concise and assumes first order diffusional kinetics overall. The parameter D_0 [m²/s] can be considered as a pre-exponential factor of the diffusion coefficient.

$$\omega_2 = \omega_{2,0} \left(1 - \exp \left(- \frac{D_0 \exp(-E_a/RT)}{r_0^2} \right) \right) \quad (2)$$

3. Results and conclusion

Following dissolution experiments of plasticised PVC in N-methyl pyrrolidone (NMP), cyclohexanone, 2-methyltetrahydrofuran (2-MeTHF) and methyl ether ketone (MEK), the model parameters are fitted against the

experimental data. Three different particle sizes (1090 μm , 2190 μm , 2990 μm) and three different temperatures (30 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$) were evaluated and for each, the mean relative error (MRE) is calculated. This statistical tool shows how each model performs under the experimental conditions, of which a spider plot is given in Figure 1.

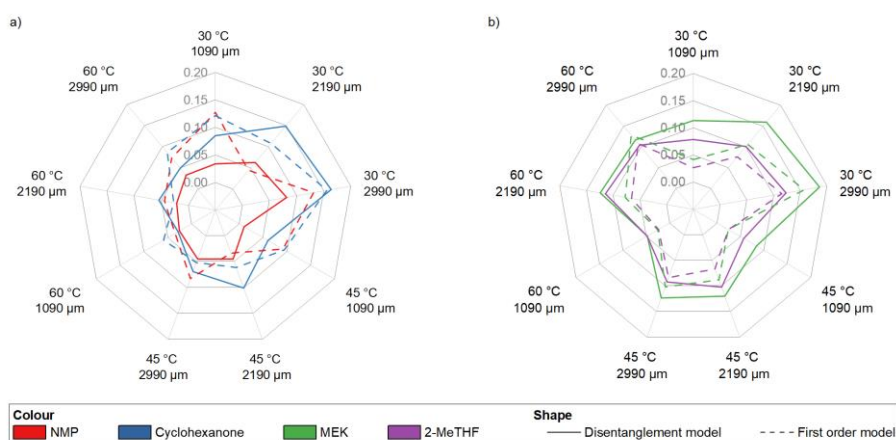


Figure 1: A spider plot of the mean relative error (MRE) of the disentanglement model and the first order model, obtained from (Denolf et al., To be published).

The first order kinetics model provide a globally better description of the dissolution profiles for MEK and 2-MeTHF, while it does not for NMP. This leads to the possibility that the chain disentanglement model, within these experiments, seems to be more suitable for the description of good to very good PVC solvents like NMP and cyclohexanone. The chain disentanglement model for NMP is significantly better at describing the dissolution profile at temperatures around or below the glass transition temperature of the polymer sample, which lies around 45 $^{\circ}\text{C}$. This difference was less pronounced at higher temperatures. The plasticiser was observed to dissolve equally as fast, if not faster than the PVC sample. It can be concluded that both models are able to predict the experimental data with reasonable accuracy whilst also being easy to work with. The MRE calculation shows that the first order model is in general more suitable for less performant solvents, whilst the opposite is true for the disentanglement model. However, in order to obtain more precise and accurate models, more fundamental research is needed. An expression for the disentanglement rate derived on first principles still lacks as well as the understanding of molecular dynamics of additives in polymer dissolution. These insights could be of tremendous value in design and operation of solvent-based recycling processes, making a circular economy for plastics possible.

4. References

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