

Influence of Plasticizers on the Diffusion of Solvents in Polymers

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Presented at the 15th International Coating Science and Technology Symposium,
September 13-15, 2010, St. Paul, MN¹

Abstract

In many cases, the diffusion of organic solvents in polymeric solutions limits the drying rate in a process. It is known, that the concentration of the solvent in the solution has a significant influence of the diffusion coefficient. The effect of small amounts of plasticizers in the polymeric solution mixture on the diffusion coefficient of the solvent are often neglected. In this work, the influence of plasticizer Triphenylphosphat on the mutual diffusion coefficient of Methylenchlorid in the system Methylenchlorid-Triphenylphosphat-Polyvinylacetate was determined. The results showed that small amounts of plasticizer have significant influence on the diffusion coefficient of solvents in the polymeric coatings – especially at low solvent concentrations.

Introduction

For a careful description of drying process, information about mutual diffusion coefficients of the solvents in polymeric systems is the main issue. Although this information is so important, only few reliable diffusion data are available in literature. In addition, most of the polymeric solutions applied in industry contain non-volatile additives like plasticizers, flame retardants or UV stabilizers, but the influence of such additives on the solvent mobility in polymeric systems is not investigated so far. For this investigation, a new approach to determine the mutual diffusion coefficients of solvents in polymeric systems is applied. Results showed that small amounts of plasticizer can have significant influence on the mutual diffusion coefficient of solvents in polymeric coatings.

Method

An established method to measure mutual diffusion coefficients was proposed by Crank [1] and is based on gravimetric experiments in which the diffusion coefficient of the solvent in the polymer can be determined from the sorption kinetics. This approach has been successfully applied in many works to determine mutual diffusion coefficients of solvents in polymeric solutions [2, 3]. A method proposed by Price et al. [4] is that mutual diffusion coefficients were determined by correlating simulations to results of gravimetric drying experiments. In this work, an new approach bases on the idea to measure the local solvent concentration profile within the polymeric film during the drying process and then determine the

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diffusion coefficient of the solvent by fitting simulation results to the experimental data. In contrast to integral gravimetric values of the entire film, concentration profile measurements provides all necessary information in order to fit the evolution and changes of concentrations in a film as a function of space and time by diffusion in the film. These measurements were performed with the Inverse-Micro-Raman-Spectroscopy (IMRS) [5] showed in figure 1. The IMRS-measuring technique is located below a flow channel, in which the polymeric coatings were cast on a thin glass plate and isothermally dried. Through a thin glass plate, the non-invasive measuring technique is able to detect the local chemical composition within the polymeric film with a spatial resolution of ca. 1 μm and an integration time of about 0,5 to 1 second.

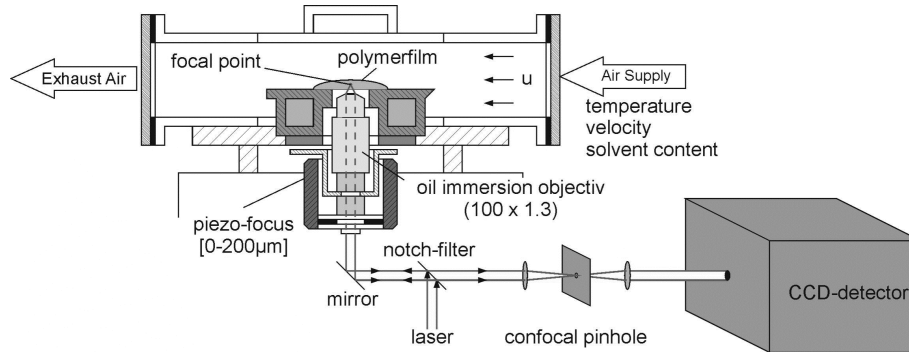


Figure 1: Setup of the Inverse Micro Raman Spectroscopy for the experimental investigation of the solvent concentration profiles during the diffusion and drying process.

For the simulation of the drying process, a program developed by Schabel et al. [6] was used, which is able to describe the mass transport within the polymeric film as well as the sorption equilibrium at the phase boundary and the mass transport in the gas phase. In order to describe the solvent diffusion as a function of solvent content and plasticizer content an empirical and “easy to use” exponential approach is proposed here and applied to describe the mutual diffusion coefficient of the solvent in the polymeric system as a function of solvent content. In equation (1) D is the mutual diffusion coefficient of the solvent, X_1 the solvent content in $\text{g}_{\text{Solvent}}/\text{g}_{\text{PVAc}}$ and a , b and c are parameters that have to be fitted to the experimental data. Parameters a , b and c itself are a function of the plasticizer content.

$$D = \exp\left(-\frac{a + b \cdot X_1}{1 + c \cdot X_1}\right) \left[\frac{\text{m}^2}{\text{s}}\right] \quad (1)$$

Parameters a , b and c are the only unknown variables in the simulation. By fitting the calculated to the measured solvent content profiles, the parameters a , b and c of equation (1) are determined.

Results and discussion

As a “solvent-plasticizer-polymeric” model systems the solvent Methylenechlorid (MeCl), the plasticizer Triphenylphosphat (TPP) and the polymer Polyvinyl Acetate (PVAc) was investigated. The influence of plasticizer content on the diffusion mobility of the solvent has been investigated at in drying experiments with plasticizer contents of 0%, 5%, 10 % and 15 % $[\text{g}_{\text{TPP}}/\text{g}_{\text{PVAc}}]$. The investigated drying temperature was adjusted to 20°C and the air flow velocity to $u = 0.2 \text{ m/s}$. The results of such a drying experiment at a TPP content of 15 % $[\text{g}_{\text{TPP}}/\text{g}_{\text{PVAc}}]$ are presented in figure 2. In the diagram on the left hand side, the measured local solvent contents (dots) are plotted against the position within the polymeric film.

At the beginning of the drying experiment, the film has an initial solvent content of $X_{\text{MeCl}} = 0.9$ $[\text{g}_{\text{MeCl}}/\text{g}_{\text{PVAc}}]$ and a thickness of 115 μm . In addition to the measured solvent content profiles, the

simulated profiles are plotted in the diagram. The diffusion coefficients are obtained by fitting calculated to the measured profiles. Figure 2 shows that the measured solvent content profiles are predicted very well with the fitted diffusion coefficients described by equation (1) (determined parameters a, b and c). On the right hand side of figure 2, the average solvent content of the film is plotted against time (which is known as a drying curve, obtained by gravimetric methods). The calculated and experimentally determined integral drying curves are as well perfectly matched, which is actually obvious, if the local profiles in the film are already fitted.

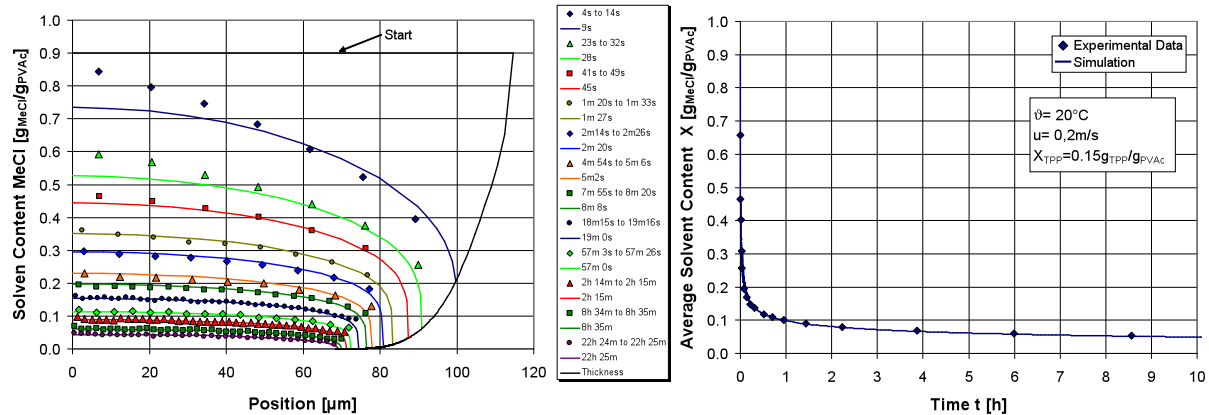


Figure 2: Measured (points) and simulated (lines) MeCl content during the drying process of a MeCl-TPP-PVAc film with a TPP content of 0.15 g_{TPP}/g_{PVAc} at $\vartheta = 20^\circ\text{C}$ and $u = 0.2\text{m/s}$. Left: local MeCl profiles in the film. Right: Average MeCl content in the film as a function of time (corresponding to a integral drying curve).

The drying curve is shown here for 10 hours of the drying experiment (Measured and simulated). These drying experiments were repeated with the polymeric solution with different plasticizer contents. The results are presented in figure 3, where the drying curves of the different solutions are shown.

It could be shown, that the plasticizer content has a minor influence on the drying rate at the beginning of the experiments, which indicates that phase equilibrium and sorption behavior of solvents is not influenced by the plasticizer content. Between solvent contents of $X_{\text{MeCl}} = 0.9$ and 0.2 [g_{MeCl}/g_{PVAc}] the four drying curves are nearly identical.

In the initial constant rate period the drying rate is controlled by the gas phase mass transport resistance and not by solvent diffusion in the polymeric coating.

Below ca. 20 % solvent content [0.2 g_{MeCl}/g_{PVAc}] the falling rate period here begins, in which the drying rate is limited by the solvent diffusion in the film. In this region, the drying curves of the different plasticizer mixtures starts to deviate from each other. The solvent mixture with the highest TPP content (15%) has the highest drying rate - the solvent with no TPP (0 %) the lowest.

As an example to emphasize this effects, e.g. in order to reach a residual solvent content of 6 % [g_{MeCl}/g_{PVAc}] the coating with 15 % TPP requires a drying time of ca. 6 hours.

Without any plasticizers (0 % TPP), the drying time extends to more than ten times higher (65 hours!). This shows the importance of taking into account the influence of plasticizer content on the diffusion coefficients besides taking into account the influence of solvent contents by e.g. Free Volume Theory.

Particularly for diffusion processes in polymeric coatings at low solvent contents in the final drying stages.

Acknowledgement

The Authors would like to thank the DFG (German Research Foundation) for financing this project

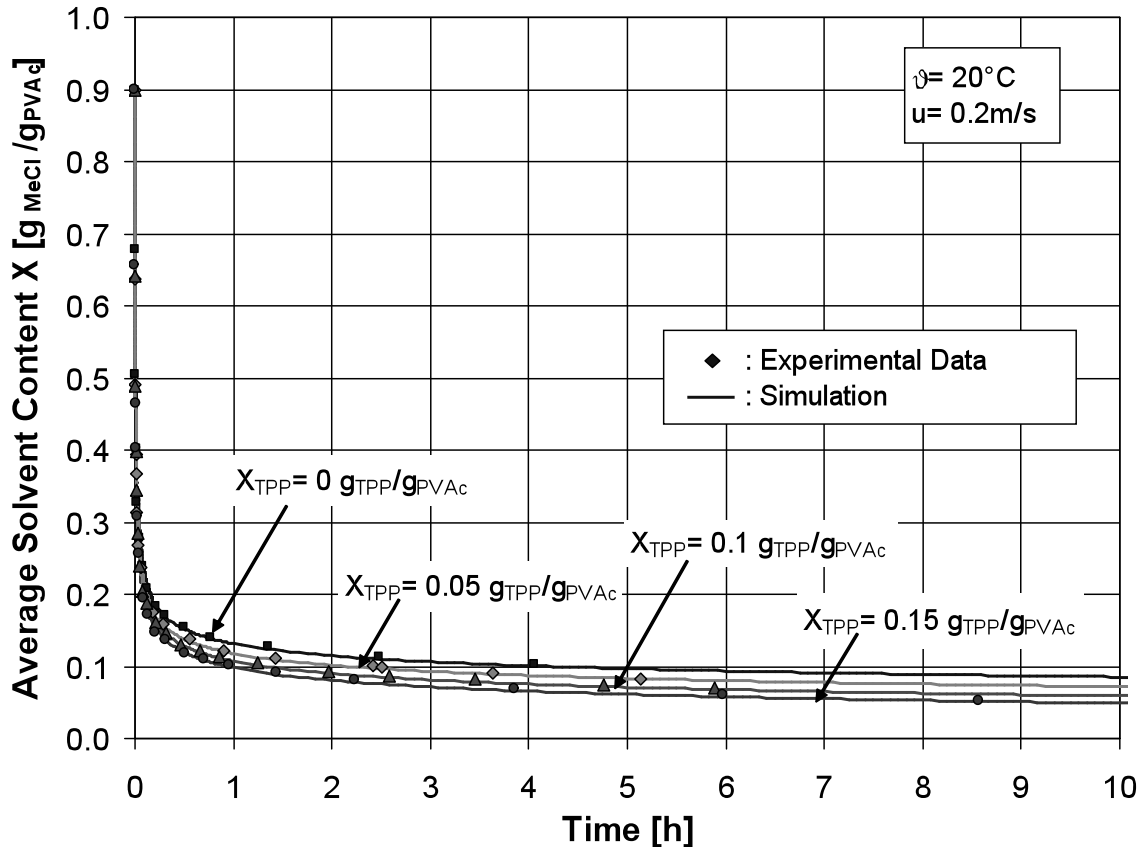


Figure 3: Measured (points) and simulated (lines) drying curves of MeCl-TPP-PVAc solutions with TPP contents of 0%, 5 %, 10% and 15 % [g_{TPP}/g_{PVAc}] ($\vartheta = 20^{\circ}C$, $u = 0.2m/s$).

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