

Diffusion of Non-Volatile Species in thin Polymeric Coatings

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Introduction

Polymeric films for modern products like LCD-panels, transdermal patches or medical test strips typically consist of a polymer and one or more non-volatile additive (e. g. plasticizers, drugs or surfactants). During the production process (casting and drying the multi-component solution), diffusion of solvents and non-volatile species in polymeric systems plays an important role. Recent experiments revealed that the drying conditions can have a significant influence on the formation of inhomogeneous additive distribution in the final product. For the multicomponent system, Cellulosetriacetat (TAC, polymer), Triphenylphosphat

(TPP, plasticizer) and Methylenchlorid (MeCl solvent), typically used in the production of LCD-panels protection foils, could be shown that the residual non-volatile components are not homogeneously distributed in the dry foil. In figure 1, the plasticizer loading is shown for different drying condition. The diamonds represent the plasticizer loading

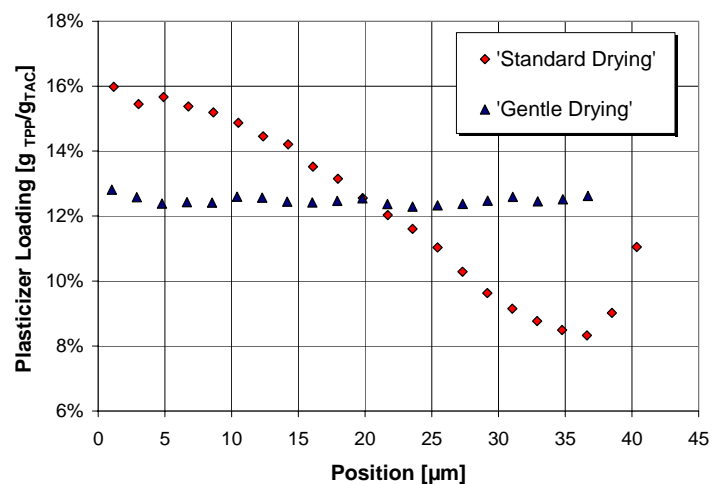


Figure 1: Influence of the drying conditions on the plasticizer distribution in the final foil

distribution after 'standard' drying (according to industrial processes), the triangles represents the final plasticizer distribution dried very gentle. Since the plasticizer is mainly responsible for the desired

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mechanical and optical properties, water vapor permeability and scratch resistance of the foil, an inhomogeneous distribution in the product can lead to severe quality problems. The diffusion phenomena, which lead to the formation of additive profiles in the dry foil, have not been investigated in detail in the literature so far. To describe the diffusion of the non-volatile species in the multicomponent polymeric system, reliable information about the influence of the solvent concentration and the temperature on the mobility of the additive is essential.

Experimental and Results

To determine the mobility of the additive in the polymer system as a function of solvent concentration and temperature, a model system (Polyvinyl acetate (PVAc), TPP and MeCl) was chosen and two types of experiments were performed and observed with the Inverse-Micro-Raman-Spectroscopy (IMRS). To get information about the influence of the solvent on the diffusion rate of the non-volatile additive, two MeCl-PVAc solutions - one with and one without the non-volatile additive (TPP) - were casted on two thin glass plates and were stuck together. After the two films have contact with each other, the additive concentration gradient between both films equalizes by diffusion of the additive. This equalization

process is investigated with the Inverse-Micro-Raman-Spectroscopy (IMRS), which provides quantitative information of chemical compositions in multi-component mixtures. Since the polymeric solution layer is covered on both sides with glass slides, the solvent concentration stays constant during the experiment. In figure 2 the result of such an experiment is shown. The dots represent the

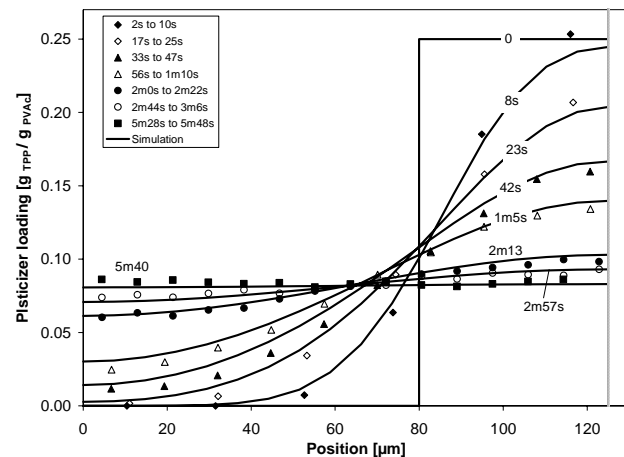


Figure 2: Results of a Two-Layer-Experiment:
Dots: Experimental data; Lines: Simulation

measured plasticizer loading during the equalization process. With the results of these experiments and a suitable simulation, the diffusion coefficient of the additive in the polymeric solution can be determined by fitting the calculated additive profiles to the experimental data (see figure 2). Thereby, it is assumed as a first approximation that the diffusion coefficient of the plasticizer in the polymeric solution is only a

function of the solvent concentration, which stays constant during the experiment. Since the simulated and measured additive concentration profiles are in good agreement, this assumption seems to be acceptable in the observed solvent/additive loading range. The comparison between simulated and measured profiles shows, that the simulation represents the experimental data with only small deviations. By performing these Two-Layer-Experiments at different solvent concentrations, one obtains the diffusion coefficient of the non-volatile plasticizer in the polymeric system in a solvent content range, where the solution still can be casted on the substrates. Below a certain solvent concentration, these experiments can not be performed any more. Because of the low viscosity of solution, the two films do not form a continuous layer where the diffusion of the plasticizer can be observed. But especially in case of very low solvent content the characterisation of the influence of solvent concentration on the mobility of the plasticizer is crucial for the latter stages of the drying process and the properties of the final product. Therefore, a new experimental setup was designed and experiments were performed with special polymeric films which were produced in two steps. In a first step, a thin film, consisting of solvent, plasticizer and polymer is coated and dried on a glass slide. In a next step, a second layer of polymer solution without plasticizer is coated above the first layer and subsequently dried. The film should be dried as fast as possible after the application of the second layer, in order to prevent equalization of the plasticizer concentration in both layers by should have as little time as possible to diffusion. Once the film is dry, the plasticizer concentration profile in the film is 'frozen' and it can be stored at ambient temperatures for a long period (proved in our lab more than 3 years) without equalisation of the profiles. Due to this low mobility, it is almost not possible to determine the diffusion coefficient by measuring the equalisation process at low temperatures (near glass transition) which would be necessary for an entire characterisation of the mobility of the plasticizer. With increasing temperature, the plasticizer becomes more mobile and the equalisation process of the plasticizer in the film can be observed in acceptable experimental time. The diffusion coefficient of the additive in the polymeric film is again determined by fitting the calculated additive profiles to the experimental data. These experiments were performed at different temperatures to obtain the diffusion coefficients of the plasticizer as a function of temperature. The corresponding results are shown in figure 3. With the experimental data and the William-Landel-

Ferry-equation (WLF), which describes the dynamics of polymeric systems as a function of temperature, it is possible to predict the diffusion coefficient of the plasticizer in the polymer at lower temperatures (see plot in figure 3). With the results of the experiments described above, the influence of solvent concentration on the diffusion coefficient of the plasticizer in the polymeric solution can be characterized.

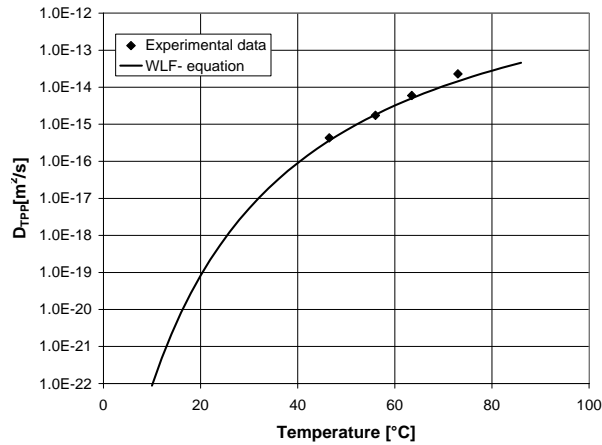


Figure 3: Influence of the temperature on the diffusion coefficient of TPP in PVAc

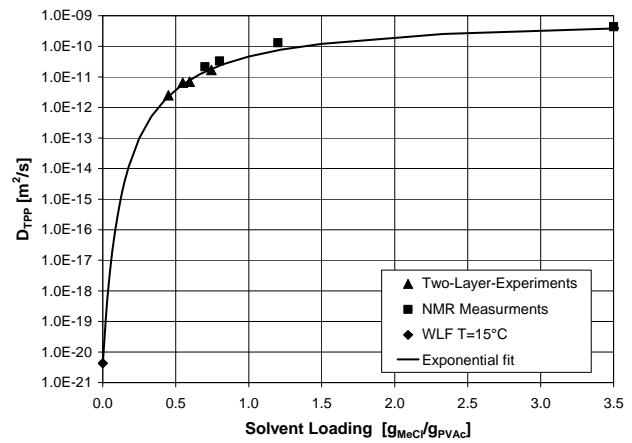


Figure 4: Influence of the MeCl loading on the diffusion coefficient of TPP in PVAc solution at 15°C

In a first attempt, the experimental data were fitted with an exponential function which is plotted together with the measurements in figure 4. In addition to the described experiments, the diffusion coefficient of the plasticizer was also determined by NMR-measurements which are also plotted in the diagram.

Outlook

Goal of the presented experiments is to get reliable data for the description of the diffusion of non-volatile components in polymeric systems and implement this information in simulation to describe the inhomogeneous distribution of the non-volatile components in the final foil. Comparing the predicted concentration profiles with profiles measured by IMRS will be a rigorous test of various multi component diffusion theories and should enable to improved existing diffusion theories or validate new ones. New model approaches combined with such experimental investigations are key issues for further developments in the field of multi component diffusion in polymeric systems especially with non-volatile species.

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