Diffusion in Multi-Component Polymeric Systems: Diffusion of Non-Volatile Species in thin films

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There are many newly established industrial applications, where diffusion of solvents and non-volatile species in polymeric systems plays an important role for the process and affects desired product properties. Examples include modern products as foils for LCD-panels, transdermal patches or medical test strips and membranes for gas or liquid separations. The distribution of the non-volatile components in the final film has an important impact on the physical and chemical properties, including mechanical and optical properties, wetting behavior or drug release rates i.e. the product quality of the polymeric system.

Typically, the multi-component mixtures for these technical applications, consisting of polymer with more than one solvent and more than one non-volatile component (additives like plasticizers, drugs or surfactants), are casted on a substrate and dried afterwards. During investigations of the drying behavior of such a multicomponent polymeric solution it was observed, that the residual non-volatile components (polymer and additive) were not homogeneously distributed in the dry foil but formed a distinctive profile of the additive content (see figure 1). Investigation of industrial produced foils with the same formulation showed the same distribution. The existence of these inhomogeneities in thin foils is often not known by the producers and can cause severe quality problems. These diffusion phenomena are neither considered nor described by existing model theories and has not been investigated in detail in the literature so far.

Further experiments revealed, that the drying conditions have a significant influence of the formation of the inhomogeneous distribution of the non-volatile components in the final foil. In figure 1, the results of such drying experiments are shown. The light dots represent the plasticizer content in the final foil, dried at “standard” conditions (fast), the dark dots represents the final plasticizer distribution dried at very gentle drying conditions. These results clearly reveal, that changing the solvent fluxes in this multi-component system leads to different mass transfer and influences the diffusion of the non-volatiles and hence the formation of the plasticizer profile in the final film.

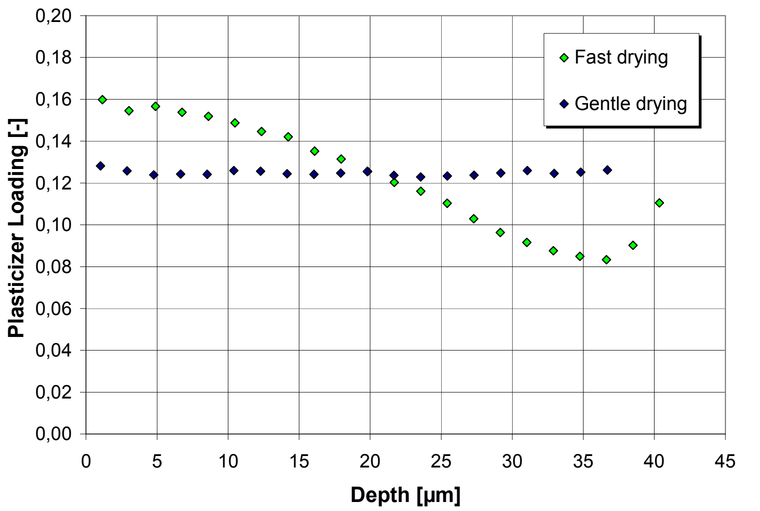

Figure1: Influence of the drying conditions on the plasticizer-distribution in the final foil

To be able to describe the drying process and to explain inhomogeneous distribution of non-volatile components in the final foil, the diffusion of the solvent in the polymeric solution must be taken into account as well as the mobility (i.e. the diffusion) of the non-volatile additive. For a correct simulation of the diffusion process in the multicomponent polymeric system, reliable and accurate data, which describe the diffusion behavior of the solvent and the additive in the polymer, are essential.

In the case of solvent – polymer – interaction, required data like sorption isotherms and diffusion coefficients can be obtained by means of a sorption balance. With this established method, the influence of the present of the additive on these data can also be investigated. To get information about the mobility of the additive in the polymeric solution new experiments and measuring techniques are needed. Therefore the so called "Two-Layer-Experiments" were performed. Two polymeric solutions - one consisting of polymer, solvent and additive (plasticizer), the other consisting of only polymer and solvent - 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 an innovative experimental technique, the Inverse-Micro-Raman-Spectroscopy (IMRS), which provides the possibility to detect chemical compositions in multi-component mixtures locally and contact-free. 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 measured ones. These calculations were not performed yet, but to be able to compare different experiments with each other, a measure for the progress of the equalization process was defined by forming the maximum difference of the additive loading within the film. By plotting this difference of each measurement against the time when the measurement was performed, one obtains the progress of the equalization of the additive loading as a function of time. When the difference becomes zero, the additive gradient has been equalized in the film. These plots can be used to compare different experiments. Figure 2 reveals the influence of the solvent loading on the mobility of the additive in the polymer solution. The diagram shows a significant increase of equilibrium-time (i.e. decrease of additive mobility) with decreasing solvent loading. By means of these experiments, the influence of temperature and the choice of solvent on the mobility of the non-volatile plasticizer in the polymeric solution will also be investigated.

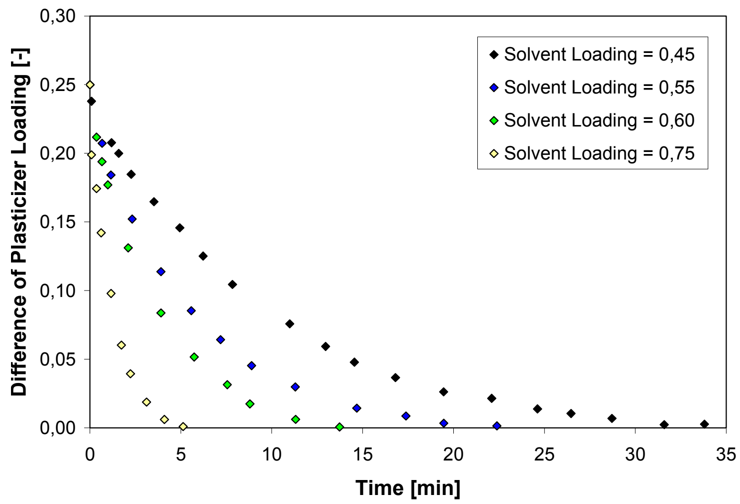

Figure2: Influence of the solvent loading on the mobility of the plasticizer in the polymeric solution

Goal of these experiments is to get reliable data to be able to describe 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.

New approaches combined with precise experimental investigation and measurements in thin polymeric films are key issues for further developments in the field of diffusion in polymeric systems especially with multi-components. In addition to the above mentioned applications, simulation of diffusion in polymeric systems has been beneficial for improving the drying process of polymeric solvent coatings.